

## FOREWORD

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## ABSTRACT

The infrared absorption spectra of 191 polymers, resins, waxes, plasticizers, monomers, and solvents have been investigated from 700  $\text{cm}^{-1}$  to 250  $\text{cm}^{-1}$ . The absorption bands of the more important chemical families were incorporated into correlation charts. The structure of the substances investigated are discussed with respect to their infrared spectra.

This technical documentary report has been reviewed and is approved.

*Freeman F. Bentley*

FREEMAN F. BENTLEY  
Chief, Analytical Branch  
Materials Physics Division  
AF Materials Laboratory

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## I. INTRODUCTION

The great value of infrared spectroscopy in the structure elucidation and analysis of technical polymers and resins has been well established. Hausdorff<sup>1</sup> and Kagarise and Weinberger<sup>2</sup> were the first to publish collections of infrared spectra of technical polymers and resins. Krimm<sup>3</sup> studied eight different polymers. He made a complete vibrational analysis of these compounds and proposed possible structures. Hummel<sup>4</sup> has published two books on polymeric materials. One book contains a comprehensive and systematic collection of spectra; the other enumerates distinguishing spectral characteristics of these compounds. In 1961, Brown et al<sup>5</sup> and Nyquist<sup>6</sup> published spectral data on newly synthesized polymers and resins.

All of the aforementioned authors' studies of polymers were limited to the NaCl range between 5000 - 667  $\text{cm}^{-1}$ . This present paper reports the results of a study of polymers, resins, waxes, plasticizers, and monomers in the region of 700 - 250  $\text{cm}^{-1}$ .

For the spectroscopist who is interested in molecular vibrations of polymers in terms of group theory and normal coordinate treatment, the authors who have discussed these topics are listed in the reference portion of this report.<sup>3,8-15</sup>

To date, there has been only one publication on the reflection of plastics in the far infrared.<sup>15</sup> The spectrophotometer used was rather simple. Reststrahlen filters were used to produce monochromatic radiation and transmittance and reflection were measured near 480, 340, 240, 195, 160, 120, 105, 80, and 60  $\text{cm}^{-1}$ . The spectra depicted in the article were so small that it was impossible to observe any bands unique to the

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plastics recorded. Spectra in the far infrared are sensitive to slight changes in structure and often contribute valuable information in identifying complex molecules and mixtures. Moreover, each additional absorption band in the far infrared complements the structural information already obtained with the rocksalt spectrum and results in a more reliable identification of a system.

Absorptions in the far infrared are mainly due to bending vibrations of the skeleton and to stretching and bending vibrations of heavy atoms such as the halogens, silicon or metals. The transition energies are low, and interactions within and between molecules may have a strong influence on the frequency and intensity of certain absorption bands. This implies a sensitivity of far infrared spectra to the physical state of a substance and the conformation of its molecules. This is advantageous where polymers with the same chemical structure but different conformation (tacticity) or crystallinity must be analyzed. On the other hand, strong but random interactions within and between polar molecules are clearly disadvantageous from an analytical aspect since they tend to produce a strong absorption background and a broadening of the absorption bands. All these factors affecting spectral features in the far infrared will be more fully explained in succeeding paragraphs.

As was mentioned previously, there are interactions within and between molecules which can affect a spectrum. These are intra- and intermolecular interactions. The former is initiated by mechanical as well as electrical coupling; the latter is usually of an electric nature: dipole-dipole interactions and van der Waals forces.

An example of very strong forces between the molecules is that of polyamides (polymers with intermolecular hydrogen bridges). Intermolecular

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forces are strongest in crystalline polymers. The vibrations in one molecule or monomer unit cannot be discussed without consideration of the same vibrations in the neighboring molecule or monomer unit. This close association between the molecules causes the well-known splitting of certain bands of crystalline polymers.

A well-known example of the influence of intramolecular interaction is the carbonyl stretching vibration. Its frequency position and intensity depends principally upon the polarity of the intramolecular environment. Weaker forces usually have too small an influence to be observed with bands of higher energy. However, the vibrations in the far infrared have a low vibrational energy and are much more liable to change in frequency position or intensity by weak forces. This influence is strongly heightened by a symmetrical conformation of the polymer chain, i.e., the repeating units being in the same plane or in an n-fold helix.

Crystallinity always causes a certain symmetry within the chain. However, isotactic and syndiotactic configuration of a polymer usually force the monomer units into a symmetrical arrangement independently of three-dimensional crystallinity. Isotactic configuration of the asymmetric carbon atoms in a chain frequently produces a helical conformation in the chain. This conformation may be considered as a one-dimensional crystallinity, and may exist even in an amorphous sample. Both effects have their influence on a spectrum. It is therefore possible to distinguish between "crystalline" (in the sense of three-dimensional crystallinity) and "tactic" absorption bands. The former ones disappear in molten or dissolved material, the latter ones remain if the conformation within the chain is unaltered during the melting or dissolving process. Polystyrene is a good example of a polymer which exhibits these effects. The bands at  $565\text{ cm}^{-1}$

# Conclusions

and  $498\text{ cm}^{-1}$  of the crystalline material are very weak or disappear in dissolved or swollen isotactic polystyrene. These bands are apparently sensitive to crystallinity. On the other hand, an absorption band at  $588\text{ cm}^{-1}$  is the same in the spectra of crystalline and amorphous isotactic polystyrene. It is not observed in the spectrum of atactic polystyrene. This band is apparently specific for isotacticity and is caused principally by intramolecular interactions.

As to the intensity of far infrared absorption bands, polymers and resins can be classified roughly into three groups. The first group includes molecules containing heavy polar atoms. Examples are halogenated polyhydrocarbons and silicones. These compounds have polar bonds and give rise to very strong absorption bands. Their spectra in the long wavelength region may be recorded as films  $0.005$  to  $0.01$  mm in thickness. The second group comprises practically all compounds with less heavy and polar heteroatoms like oxygen and nitrogen. Aromatic structures also are included in this group. Examples are polyesters, polyethers, phenolic resins, amino and amido resins, and aromatic polyhydrocarbons. These compounds give rise to absorption bands of medium intensity. Sample thicknesses around  $0.1$  mm are needed to obtain significant spectra. The third group consists of compounds having only structures of low polarity. Examples are aliphatic polyhydrocarbons of all kinds. These molecules usually have only weak absorption bands in the far infrared. Sample pathlengths between  $0.3$  mm and several millimeters are needed. The lower value holds for polymers with high sterical order, especially crystalline ones.

## II. EXPERIMENTAL

### A. Apparatus

The spectra shown in this report were recorded with a Perkin-Elmer Spectrophotometer Model 102 described by Marshall.<sup>16</sup> To reduce the loss of energy due to atmospheric absorption, the entire instrument was purged with dry nitrogen. The wavenumber reproducibility is  $0.5 \text{ cm}^{-1}$  over the entire range.

In the present work, many of the spectra of samples were scanned using devices such as screens or cells with paraffin oil or solvents in the reference beam to compensate for absorption background and scattered light. Therefore, these spectra can only be used on a qualitative basis since the transmittances may not be true.

(indicated by x on spectrum)

Sometimes water bands are evident in the spectra/even though purging of the instrument with nitrogen was carried out. These are not to be confused with sample absorption bands. Therefore, a spectrum of water vapor is depicted in Figure 1 and band positions are enumerated in Table 1.

### B. Materials

Most of the materials used were contributed by the manufacturers and are of a technical grade. The plasticizers and monomers originated partly from a collection owned by the Monsanto Research Corporation, Dayton, Ohio, and partly from the Institut für Physikalische Chemie und Kolloidchemie, University of Cologne, Cologne, Germany. All of the eutactic polymers, with the exception of isotactic polypropylene, were research samples contributed by Rohm and Haas Gmb H, Darmstadt, Germany, and by Monsanto Chemical Company, St. Louis, Missouri. The solvents used were analytical grade.

TABLE I  
Far Infrared Absorption Bands of Water Vapor\*

Wavenumber (cm <sup>-1</sup> )	526.23	502.45	472.68	458.05	443.90	442.24	436.64	425.42
Wavelength (μ)	19.003	19.902	21.156	21.832	22.528	22.612	22.902	23.506
Wavenumber (cm <sup>-1</sup> )	423.14	397.81	394.51	374.80	370.26	354.47	351.88	349.92
Wavelength (μ)	23.633	25.138	25.348	26.681	27.008	28.211	28.419	28.578
Wavenumber (cm <sup>-1</sup> )	343.38	335.34	328.34	327.78	323.90	303.30	303.00	302.04
Wavelength (μ)	29.122	29.820	30.456	30.508	30.874	32.970	33.003	33.108
Wavenumber (cm <sup>-1</sup> )	290.91	289.65	282.45	280.46	278.55	276.29	267.73	266.94
Wavelength (μ)	34.375	34.524	35.404	35.656	35.900	36.194	37.351	37.462
Wavenumber (cm <sup>-1</sup> )	266.29	254.06	248.01	245.65	227.93	226.38	223.82	221.74
Wavelength (μ)	37.553	39.361	40.321	40.708	43.873	44.174	44.679	45.098

\*These bands are found in the work of Randall et al.<sup>17</sup> and only the most intense are reported here.  
The accuracy is 0.05 cm<sup>-1</sup>.

## C. Preparation of Samples

The infrared spectra of polymers studied in this report were obtained as films cast from solutions, pressed or melted films, microtomed samples, paraffin oil mulls or as KBr disks.

### 1. Films Cast from Solutions

The majority of the polymers studied were recorded as films. The films were prepared by dissolving these compounds in a suitable organic solvent (see individual spectra for solvent used), pouring them onto a glass plate and evaporating off the solvent. If the films adhered too tightly to the surface of the glass, they were heated with water until they could be drawn off.

Resins were cast directly on cesium bromide plates approximately 5 mm in thickness. To check if interfering bands were present due to these plates in the region of  $700\text{-}250\text{ cm}^{-1}$ , a spectrum was recorded (Figure 2). Cesium bromide used in these studies was found to be transparent in this range.

In the case of polyamides, films were difficult to cast and handle. Formic acid was used as a solvent, and opaque and nonuniform films resulted. To correct this, these films were soaked with paraffin oil while still on the glass plate and then carefully removed with the help of a razor blade to a cesium plate. The spectra of the samples were recorded and compensation for the paraffin oil adhering to the film was made by placing an equivalent amount of oil on a CsBr plate in the reference beam.

Polymers, like polyoxymethylene, were dissolved in dimethyl sulfoxide. Then they were precipitated from a methanol or ethanol solution. The precipitate was washed at least five times to remove the high boiling solvent

and then dried in a vacuum oven to remove the alcohol. The resultant dried powder was prepared for recording by using either KBr or mulling techniques.

Polymers often retain the solvents used to prepare films. Drying in a vacuum oven at elevated temperatures most of the time was sufficient to drive them off. Sometimes, however, extraction with a low-boiling non-solvent for the polymer had to be employed. Water was found to be an efficient extractant for dimethyl formamide, dimethyl sulfoxide, anhydrous ethanol, and benzene.

## 2. Pressed or Melted Films

Non-polar polymers, like polyethylene, require sample thicknesses up to a few millimeters in order to obtain a significant spectrum. Films of these thicknesses are best prepared in a die, heated at a temperature about 20°C above the softening temperature of the polymer. Since many polymers will oxidize at higher temperatures, the pressing should be done in an inert atmosphere. If a high degree of crystallinity in the polymer sample is desired, the cooling is done quite slowly. Quenched samples can be crystallized by heating them about 20° below their melting point for a few hours.

With some caution it is possible to prepare a film between cesium bromide plates. The plates are first preheated on a heating stage to a temperature just above the melting point of the polymer. The plates are taken apart with a pair of tongs and the beads or scraps are put on one of the plates and immediately covered by the other. Pressing of the so-called sandwich with a cork, produces the desired film. Fortunately, cesium bromide and iodide are not as sensitive to sudden temperature changes as sodium chloride. However, these plates can still deform at higher temperatures and



caution must be taken when applying the technique just described.

Stereoregular poly- $\alpha$ -olefins have high melting points and are subject to oxidation. If a suitable die is unavailable, the finely divided polymer is mixed with paraffin oil into a thick slurry. The slurry is placed between cesium bromide plates and heated slowly. Part of the paraffin oil seeps out, leaving the polymer in the form of a soft, rubbery sheet. The degree of crystallinity in a sample is thus reduced by this handling procedure.

### 3. Microtomed Samples

Polymers such as vulcanized rubbers, cured polyester resins, and polytetrafluoroethylene, will not dissolve in conventional solvents or melt when heated. Consequently, these polymers, if of the right pliability, can be cut into thin slices of suitable thickness without prior treatment using a microtome. Some rubbers and very soft materials have to be cooled in a dry ice-acetone mixture to obtain a certain degree of rigidity before microtoming can be accomplished. Hard polymers are plasticized with suitable swelling agents before cutting.

### 4. Paraffin Oil Mulls

Paraffin oil or "nujol" exhibits only weak absorptions in the 700 - 300  $\text{cm}^{-1}$  region (Figure 176). This makes it an ideal carrier for finely divided compounds. Good spectra have been obtained for polyoxymethylene (Delrin), polyamides, stereoregular poly- $\alpha$ -olefins and polyvinyl chloride using the mull technique. Compensation for the paraffin oil in these samples can be accomplished by using a comparable amount of oil in the reference beam.

### 5. KBr Disks

Disks of potassium bromide are transparent to about 250  $\text{cm}^{-1}$  (40

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microns). Hence, they can be used as carriers for materials in the far infrared. Unfortunately, large concentrations of samples are often required which results in turbid or opaque disks. If compensation for the scattered light is not possible through the use of screens, a lower concentration of sample is employed and scale expansion utilized. Insoluble, hard materials can be reduced to a fine powder or shavings by scraping their surfaces with a razor blade. Devaney and Thompson<sup>18</sup> recommend the use of a diamond spatula. After the polymer is in this state, the KBr technique is applied.

## III. RESULTS

The infrared spectra of 191 polymers, resins, waxes, plasticizers, monomers and solvents have been investigated from 700 - 250  $\text{cm}^{-1}$ . All these compounds have been separated into chemically related groups and their spectra discussed in regard to their analytical use in chemical and structural problems below.

### A. Aliphatic Polyhydrocarbons (CHART I)

A thorough study of the far infrared spectra of aliphatic hydrocarbons was published by Bentley and Wolfarth.<sup>19</sup> Our findings concerning aliphatic polyhydrocarbons in this investigation are, to a certain degree, in agreement with their observations. Straight-chain paraffins of high molecular weight have just one band around 540  $\text{cm}^{-1}$  which is strong enough to be observed in samples 2 mm thick. Branched alkanes have around four bands which are stronger, intensity-wise, than the one observed for the straight chain polymers recorded at the same thickness. Hence, poly- $\alpha$ -olefins can easily be distinguished from polyethylenes.

It is important to remember that the bands found in polymer spectra are not only due to their physical state but also are the result of orientation effects. The spectra of polymers with a certain steric order within the chain, like the eutactic poly- $\alpha$ -olefins, or with a certain degree of three-dimensional crystallinity have to be discussed in terms of symmetry elements and group theory. A method for the determination of normal vibrations of polymer molecules with a helical configuration was described by Tadokoro.<sup>11,12</sup> This method is also applicable to molecules with an infinitely extended planar zigzag chain such as crystalline polyethylene.

## 1. Saturated Polyhydrocarbons

a. Polyethylene. There are two types of polyethylenes, namely, high-pressure polyethylene (low-density) and low-pressure polyethylene (high-density). The former is produced by a process developed by ICI of England and is a highly branched polymer. It contains both short (mainly  $n-C_4H_9$ ) and long side chains. The latter is produced by the Ziegler method or by other processes applying low pressures of ethylene and special catalysts. This product is unbranched.

The infrared spectra of the polyethylenes have been studied in greater detail than other polymers. However, most of the information involves the rocksalt range. A review giving the abstracts of forty-one publications on polyethylenes was reported by Wood and Luongo.<sup>20</sup> Of particular interest were quantitative methods described by several authors for identifying polyethylenes by infrared procedures<sup>21-31</sup> and by density measurements.<sup>32</sup>

Concerning the far infrared region, Rugg et al<sup>33</sup> were the first to observe weak and complex bands in the spectrum of high-pressure polyethylene with maxima at about  $591\text{ cm}^{-1}$  ( $16.9\ \mu$ ) and  $558\text{ cm}^{-1}$  ( $17.9\ \mu$ ). They gave as a probable assignment of this group of band structures the general type  $-CH_2 - CHRR'$ , R and R' being methyl, ethyl or propyl groups. Borello and Mussa<sup>34</sup> interpreted these absorption maxima and an additional band at  $543\text{ cm}^{-1}$  ( $18.4\ \mu$ ), as a pure methyl band system. Krimm et al<sup>3,31</sup> also found weak bands in the far infrared spectrum of high pressure polyethylene. Our results for polyethylenes (Figure 3) are tabulated along with Krimm's in Table 2. Tentative assignments are made for some of the vibrations.

Bands near  $630$  and  $549\text{ cm}^{-1}$  in Marlex 50 were tentatively assigned to a vibration of terminal vinyl groups. This seems reasonable since these bands were also found by Bentley and Wolfarth<sup>19</sup> in alkenes having this same

TABLE 2

Far Infrared Absorption Bands of Polyethylenes (PE)

<u>Krimm<sup>3</sup></u> (cm <sup>-1</sup> )	<u>This Report</u>		<u>Probable Assignment</u>
	<u>High-pressure PE</u> (cm <sup>-1</sup> )	<u>Marlex 50</u> (cm <sup>-1</sup> )	
---	---	630	-CH=CH <sub>2</sub>
600	---	---	---
573	585	570	---
---	---	549	-CH=CH <sub>2</sub>
543	538	---	Skeleton vibration involving CH <sub>3</sub>
---	---	450	---
430	425	430	---
200	Not studied	Not studied	---

terminal grouping. The band at  $538\text{ cm}^{-1}$  found in the spectrum of high-pressure polyethylene has already been assigned by Rugg et al.<sup>33</sup> and Borello and Mussa<sup>34</sup> as being due to a skeleton vibration involving methyl groups. Our spectral data are in agreement with their assignment based on relative band intensities at  $540\text{ cm}^{-1}$ . Branched polyethylenes show a more intense band than the unbranched. This is logical since the former contains a higher concentration of methyl groups (20 - 30 per 1000 carbon atoms) than the latter (less than 1.5 methyl groups per 1000 carbon atoms). Bentley and Wolfarth<sup>19</sup> observed a band at  $538\text{ cm}^{-1}$  in long-chain alkanes. The intensity of the band decreased with increasing chain length which is consistent with our findings above.

b. Polypropylene. Propylene can be polymerized with Lewis acids yielding low molecular weight oils or amorphous, rubberlike materials. Ziegler-type catalysts, namely, complexes of titanium halides with aluminum or beryllium alkyls, cause the formation of high molecular weight, crystalline polymers which have gained wide application in industry. These polymers have a stereoregular structure with respect to the asymmetric carbon atoms in the chain. According to Natta<sup>35</sup>, vinyl polymers with the same steric configuration, d or l, of the asymmetric carbon atoms in the chains are called "isotactic;" those with an alternating configuration of the consecutive asymmetric carbon atoms giving d, l, d, l sequences are called syndiotactic. "Atactic" vinyl polymers do not have any regularity in the distribution of the configurations of the asymmetric carbon atoms along a polymer chain. A discussion of the definition of an atactic with respect to polypropylenes was given by Folt et al.<sup>36</sup>

Cationically produced polypropylene in its structure probably comes closest to being an "atactic" polypropylene. Its infrared spectrum in the rocksalt range was discussed by Liang and Watt<sup>37</sup> and Immergut et al.<sup>38</sup> The spectrum reflects only the vibrations of a single monomer unit due to the low intermolecular forces and the random conformation of the monomer units in the chains. In the far infrared, the spectrum of "atactic" polypropylene (Figure 4) shows a broad band with maxima at  $575\text{ cm}^{-1}$  and  $557\text{ cm}^{-1}$ . These bands probably are due to the skeleton vibrations involving the methyl side-groups. Tobin<sup>39</sup> also found a broad absorption band between  $460\text{ cm}^{-1}$  and  $620\text{ cm}^{-1}$  with a maximum at  $542\text{ cm}^{-1}$  with a similar type polypropylene.

Natta and Pasquon<sup>40</sup> stated that there are three different types of stereoregular, crystallizable polypropylenes:

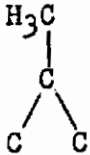
1. Isotactic head-to-tail polypropylene characterized by a helical structure of the chain with three monomer units per repeat and by a melting temperature of  $170^{\circ}\text{C}$ .

2. Syndiotactic head-to-tail polypropylene, characterized by a "double helix" of the chain with four monomer units per repeat, and by a melting temperature very close to that of the isotactic material.

3. Head-to-head and tail-to-tail polypropylene produced by alternating copolymerization of ethylene and cis butene-1.

Isotactic polypropylene is produced technically in very large quantities. It is capable of crystallizing into different polymorphous modifications.<sup>41,42</sup> However, these different forms have the same infrared spectrum. The spectra of normal protonated and deuterated isotactic polypropylenes, either crystalline or amorphous (molten or quenched), oriented and unoriented, were studied by a number of authors<sup>3,37,39,43-57</sup> in the rocksalt range. Assignment of bands to specific vibrations differ among these authors.

The only figures given to date for the far infrared absorption of isotactic polypropylene were published by Tobin.<sup>39</sup> His values, together with our findings, are shown in Table 3. An assignment for the far infrared bands of amorphous and crystalline isotactic polypropylene has not been published, but it is normal to assume that a bending vibration of the

skeleton involving the methyl side-group  is infrared active and occurs in the range of about  $450\text{ cm}^{-1}$  to  $600\text{ cm}^{-1}$ .

In the simplest case of an amorphous polypropylene with no steric order of the asymmetric carbon atoms (Figure 4), there is only one complex band, broadened by random mechanical coupling of this bending vibration with other chain vibrations. Isotactic configuration of the asymmetric carbon atoms primarily introduces a short-range order, whether helical or not, and consequently, defines interactions between the monomer units. This has a strong influence on the frequency of the C-C-C bending vibration and on its envelope, too. Usually, there is band splitting due to different phase relations of the compound (Figure 5).

Crystallinity introduces a still higher molecular order and therefore a further change in the spectrum (Figure 6). If we make the assumption that the band at  $455\text{ cm}^{-1}$  found in isotactic polypropylene is characteristic for the helical arrangement of the chains, then the band at  $527\text{ cm}^{-1}$ , occurring only in the spectrum of crystalline polypropylene, is characteristic for the phase relations in the three-dimensional crystal. If, however, the band at  $455\text{ cm}^{-1}$  is characteristic for isotactic sequences in non-helical chains, then the band at  $527\text{ cm}^{-1}$  is characteristic for a helical conformation.



TABLE 3

Far Infrared Bands of Isotactic and Atactic Polypropylenes\*

<u>Atactic</u>		<u>Isotactic, Amorphous</u>	<u>Isotactic, Crystalline</u>	
<u>Tobin<sup>39</sup></u>	<u>This Report</u>	<u>This Report</u>	<u>Tobin<sup>39</sup></u>	<u>This Report</u>
(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
-	-	315 (w)	-	312 (?) (vw)
-	-	-	408 (vw)	390 (w)
460-620 (br)	475 (?, vw)	455 (m)	460 (w)	453 (m)
-	520 (vw)	475 (m, sh)	537 (w)	527 (m)
542	557 (m)	550-575 (w, br)	580 (vw)	575 (vw, br, sh)
-	575 (m, br)	-		
		615		
-	643 (w)	-		
-	690 (w)	694		

Symbols: w = weak; vw = very weak; sh = shoulder; m = medium; br = broad.

\*The far infrared spectra of the molten isotactic polypropylene and of the syndiotactic polypropylene are not available.

# Contrails

Syndiotactic polypropylene was described by Natta et al<sup>57,58</sup> and is probably identical to the modification of polypropylene found by Addink and Beintema.<sup>42</sup> Its spectrum in the rocksalt range is very similar to that of isotactic polypropylene. It is distinguished only by a band at  $867\text{ cm}^{-1}$  not occurring in the spectrum of the isotactic material. No spectral data are available for syndiotactic polypropylene.

Disyndiotactic (head-to-head, tail-to-tail) polypropylene was described by Natta et al.<sup>58</sup> Its spectrum has not been published so far.

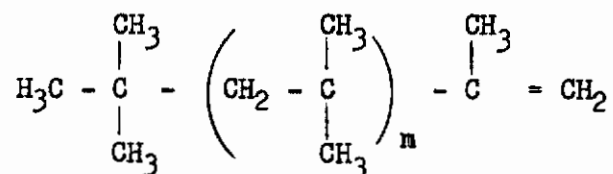
c. Polybutene-1. Complexes of titanium halides with aluminum alkyls or other catalysts described by Ziegler and Natta (see reference 35) generally polymerize 1-alkenes into stereoregular polymers. With butene-1 a crystalline isotactic polymer is formed which differs in its chemical structure from isotactic polypropylene only by the side groups, i.e., ethyl groups are present rather than methyl. The crystal structure of the most stable form of polybutene-1 was described by Natta et al.<sup>59</sup> It is very similar to that of isotactic polystyrene and isotactic polypropylene. The unit cell is rhombohedral and contains eighteen monomer units in six helices. There are three monomer units in one repeat. The strongest band at  $533\text{ cm}^{-1}$  in its far infrared spectrum (Figure 7) is probably due to the C-C-C bending vibration involving the tertiary carbon atom. A complete vibrational analysis for the spectrum of polybutene-1 has not been published.

d. Polyisobutylene. The monomer unit of polyisobutylene,

$$\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CH}_2-\text{C}- \\ | \\ \text{CH}_3 \end{array},$$
 does not contain an asymmetric carbon atom. The only possibili-

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ties of a regular structure are, therefore, head-to-tail and head-to-head tail-to-tail arrangements of the monomer units in the chains. The infrared spectra of  $\text{BF}_3$  polymerized samples were studied by Dainton and Sutherland.<sup>60</sup> According to these authors, polyisobutylene is a head-to-tail polymer with mainly tertiary butyl and isopropene groups as end groups:



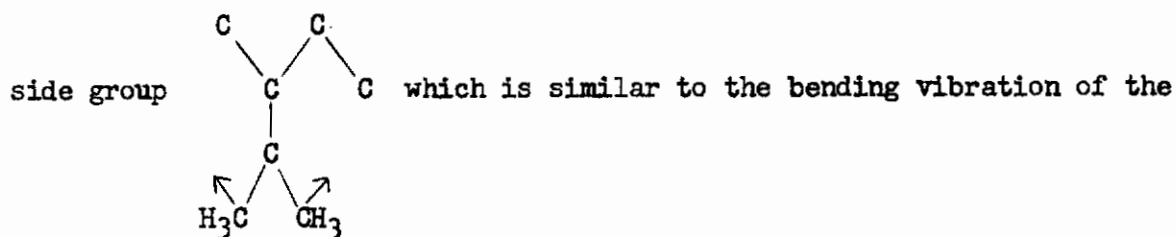
Nelson<sup>61</sup> studied the infrared absorptions of the CH groups in polyisobutylene. Fuller et al<sup>62</sup> studied the chain structure by the X-ray fiber patterns and found a fiber period of 18.63 Å. The repeating unit along the chain contains eight monomer units arranged in a helix.

The far infrared spectrum of polyisobutylene (Figure 8) shows only weak absorption bands. A band around  $510 \text{ cm}^{-1}$ , according to Bentley and Wolfarth<sup>19</sup>, is characteristic for 3,3-disubstituted alkanes. A corresponding band is found in the spectrum of polyisobutylene at  $527 \text{ cm}^{-1}$ . As other highly branched hydrocarbons, polyisobutylene shows a number of other absorption bands in the far infrared whose assignment to certain skeleton vibrations is not as yet clarified.

e. Poly(4-methylpentene-1). In certain cases, also branched 1-alkenes can be polymerized with stereospecific catalysts of the Ziegler type. Poly(4-methylpentene-1) was obtained by this process, and is a highly crystalline, high-melting polymer with an isotactic configuration of the asymmetric carbon atoms. The far infrared spectrum (Figure 9) is rather similar to that of crystalline isotactic polypropylene (Figure 6).

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It is not unlikely that this is due to a bending vibration of the isopropyl

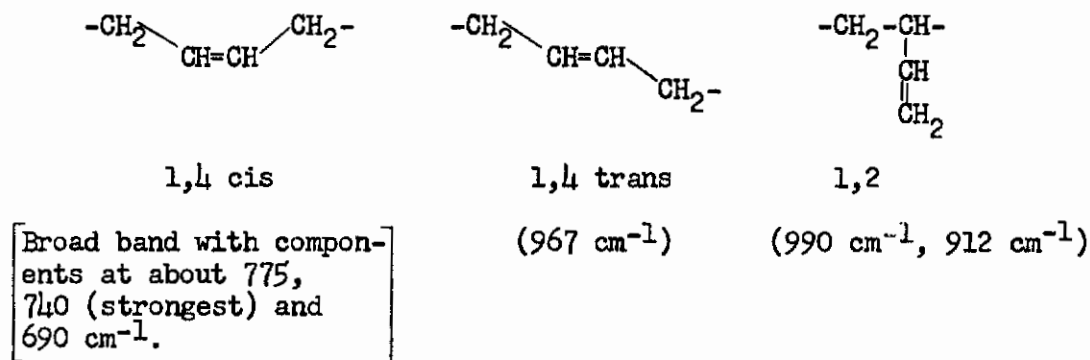


methyl side groups of amorphous and crystalline isotactic polypropylene.

Also, the splitting into three components may be due to a similar structure of the helical chains.

## 2. Unsaturated Polyhydrocarbons

a. Polybutadienes. Polybutadiene obtained with radical initiation or by other non-stereospecific catalysts contains three different steric structures in its chains:



The characteristic bands of these unsaturated groups originate from out-of-plane vibrations of the hydrogen atoms attached to the double bond (Rasmussen and Brattain<sup>63</sup>, Sheppard and Sutherland<sup>64</sup>).

The portion of the three different structures in conventional polybutadienes varies within certain limits with the kind of catalyst, and with the reaction temperature. A number of infrared spectrophotometric methods for the quantitative determination of the different monomer units in polybutadienes were published.<sup>65-72</sup> The method proposed by Kimmer and

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Schmalz<sup>71,72</sup> seems to be the best.

Conventional polybutadienes are amorphous and are either low molecular weight oils or higher molecular weight elastomers. By the application of stereospecific catalysts, butadiene can be polymerized to yield four different highly crystalline and highly stereoregular polymers: 1,4-cis; 1,4-trans; 1,2-isotactic; and 1,2-syndiotactic polybutadiene.

Preparation and properties of 1,4-cis polybutadiene were described by Natta et al.<sup>73</sup> The compound 1,4-trans polybutadiene can be obtained by certain catalyst systems<sup>74,75</sup>, or by isomerization of cis or mixed cis-trans polybutadiene under the influence of ultraviolet<sup>76</sup>, or  $\gamma$ -radiation<sup>77,78</sup> and in the presence of stabilizers. The reaction product still contains about 5 percent cis units. Crystalline 1,4-trans polybutadiene occurs in two different enantiomorphous modifications.<sup>75</sup> Nikitin et al<sup>79,80</sup> studied these modifications more closely and found a temperature range of 55-70°C for the transformation of modification I into modification II. The latter melts between 110°C and 130°C. Isotactic and syndiotactic 1,2-polybutadiene were prepared by Wilke<sup>81</sup> and by Natta and his collaborators.<sup>82,83</sup>

The infrared spectra of the stereoregular polybutadienes were studied by several authors.<sup>75,79,80,84,85</sup> Table 4 shows the infrared bands of 1,4-trans polybutadiene which are sensitive to changes in crystallinity according to Nikitin and coauthors.<sup>79,80</sup> Fairly strong bands at 9.49 and 9.93 microns mainly arise from the crystalline modification I whereas the band at 8.10 microns arises partly from modification I and partly from modification II. Table 5 shows the bands above 10 microns characteristic for isotactic or syndiotactic 1,2-polybutadienes in the crystalline state according to Morero et al.<sup>84</sup>

TABLE 4

Infrared Bands of 1,4-trans Polybutadiene\*

"Crystalline Bands"		"Amorphous Bands"	
Wavelength ( $\mu$ )	Wavenumber ( $\text{cm}^{-1}$ )	Wavelength ( $\mu$ )	Wavenumber ( $\text{cm}^{-1}$ )
7.49	1335	7.43	1346
8.10 I + II	1235	7.65	1307
8.92	1121		
9.49 I	1054		
12.93 I	773		

\*These bands are sensitive to changes in crystallinity. The Roman Numerals I and II denote the two crystal modifications.

TABLE 5

Bands Below 1000  $\text{cm}^{-1}$  Characteristic of  
Isotactic or Syndiotactic 1,2-Polybutadienes  
in the Crystalline State\*

Isotactic		Syndiotactic	
Wavelength ( $\mu$ )	Wavenumber ( $\text{cm}^{-1}$ )	Wavelength ( $\mu$ )	Wavenumber ( $\text{cm}^{-1}$ )
10.6	943	-	-
11.3	885	-	-
14.4**	694	15.0	667

\*Bands common to both were omitted.<sup>84</sup>

\*\*Also in solution, but weaker

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Golub and Shipman<sup>85</sup> were the first to investigate the far infrared absorptions of 1,4-polybutadienes and various deuterated 1,4-polybutadienes. They prepared the cis-1,4 polybutadienes by a stereospecific catalyst and the trans isomers by isomerization of the cis isomers by ultraviolet light. In Table 6, the figures found by Golub and Shipman<sup>85</sup> are compared with our own. The samples of the former authors were cast from benzene solutions. It appears from their spectra that they were amorphous. The sample of a conventional atactic polybutadiene examined in this report (Figure 10) and the sample of a high cis polybutadiene (Figure 11) were also amorphous. The 1,4-trans polybutadiene (Figure 12), however, crystallized during the drying of the film in a vacuum oven. The two sharp and distinct bands at  $440\text{ cm}^{-1}$  and  $375\text{ cm}^{-1}$  of the crystalline 1,4-trans polybutadiene (modification I) does not appear in the spectrum of a dissolved or amorphous sample, and may, therefore, also be used for the determination of crystallinity (compare Nikitin et al<sup>79,80</sup> and Table 4).

Unfortunately, amorphous cis-1,4 polybutadiene has practically no far infrared absorptions which are of any analytical value. The only analytical band for a direct determination of the cis content of polybutadienes is still that at about  $740\text{ cm}^{-1}$ .

Far infrared data of crystalline cis-1,4 polybutadiene and 1,2-polybutadienes are not available to date.

b. Polyisoprenes. 2-Substituted 1,3-butadienes of the type

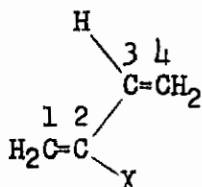


TABLE 6

Far Infrared Bands of 1,4-Polybutadienes

<u>1,4-cis</u>		<u>1,4-trans</u>		<u>Conventional Polybutadiene (mixture of isomers)</u>
<u>Golub and Shipman</u>	<u>This Report</u>	<u>Golub and Shipman*</u>	<u>This Report**</u>	<u>This Report</u>
(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
702(vw)	approx. 700(m,b)	700(w)***	-	680-730(m,b)
625(w)	580-625(w,vb)	600(vw,b)	580-600(vw,b)	580(w)
600(vw,b)				
	520(w,b)			
	470(w,b)			480(b)
			440(m)	
	390(w,b)			
			375(m)	

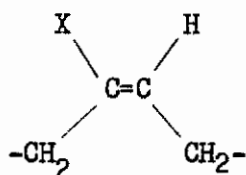
Symbols: m=medium; w=weak; vw=very weak; b=broad; vb=very broad

\*The sample was probably amorphous  
 \*\*Crystalline sample  
 \*\*\*Probably cis-isomer



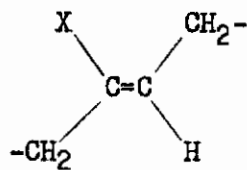
# Contrails

polymerize according to four different mechanisms, yielding four different isomeric structures:



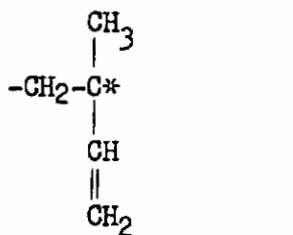
1,4-cis

(12  $\mu$ )



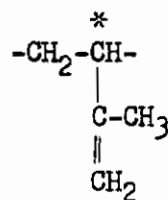
1,4-trans

(11.9  $\mu$ )



1,2

(10.1  $\mu$  and 11  $\mu$ )



3,4

(11.25  $\mu$ )

The wavelengths given for the different structures denote the absorption maxima of the hydrogen out-of-plane vibrations of the unsaturated group in amorphous polyisoprenes ( $X = \text{CH}_3$ ). The position of these maxima depends on the type of the substituent  $X$  (compare polychlorobutadiene,  $X = \text{Cl}$ ) and also on the physical state of the compound. Both 1,2- and 3,4-polyisoprenes contain asymmetric carbon atoms--in the formulas denoted with asterisks--and consequently are able to form isotactic and syndiotactic chains.

All natural polyisoprenes are 1,4-polymers and stereoregular within the chains. The band at 11.25  $\mu$  is not due to 3,4- units.<sup>86,87</sup> Hevea rubber is a cis 1,4-polyisoprene; gutta-percha and balata are trans 1,4-polyisoprenes.<sup>88</sup> Its infrared spectrum, however, is practically identical with that of gutta-percha<sup>89</sup> which is a trans 1,4-polyisoprene. All natural

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polyisoprenes contain certain amounts of resinous compounds and polypeptides; hence they must be isolated and purified prior to their spectroscopic examination.

Isoprene can be polymerized by radicals, alkali metals, "Alfin" catalysts and Lewis acids. The products obtained by these methods are not stereoregular but contain various amounts of the different isomeric monomer units in the polymer chains. The portion of these isomeric units in a polymer depends on the type of catalyst and also on the polymerization temperature. Alkali metals yield fairly uniform polymers. Sodium polyisoprene, for example, contains mainly 3,4 units. Lithium metal and aluminum trialkyl-titanium halide complexes are stereospecific and this allows the preparation of sterically uniform polymers. The first "synthetic natural rubbers" with a pure cis-1,4 structure produced in a technical scale were "Ameripol SN"<sup>90</sup> and "Coral Rubber."<sup>91</sup>

The infrared spectrum of natural and synthetic polyisoprenes was studied by a large number of authors.<sup>67,84,87,89,90-98</sup> Cis-1,4 polyisoprene crystallizes when stretched or at low temperatures. The velocity of crystallization is fastest at -26°C. The most obvious changes in the infrared spectrum during crystallization is the shift of the =C-H  $\gamma$ -vibration from 11.95  $\mu$  to about 11.8  $\mu$  and the shift of a skeleton vibration at 8.8  $\mu$  to about 8.9  $\mu$ . The absorptivity of both bands is higher in the crystalline state.

The infrared spectrum of amorphous trans-1,4 polyisoprene (gutta-percha) is very similar to that of amorphous cis-1,4 polyisoprene. The main differences are listed below:

<u>trans 1,4-polyisoprene</u>	<u>cis 1,4-polyisoprene</u>
11.9 $\mu$ , 12.4 $\mu$ (doublet)	11.95 $\mu$ (s)
-	9.9 $\mu$
8.65 $\mu$ (m)	8.8 $\mu$ (m)

Trans-1,4 polyisoprene crystallizes in two modifications. The  $\alpha$ -form is stable at room temperature, and the "natural" form of gutta-percha. It can be transformed into the  $\beta$ -form by heating the sample above 65°C and subsequent quenching. The  $\alpha$ -form is characterized by sharp bands at about 11.35  $\mu$ , 11.6  $\mu$ , and 12.45  $\mu$ ;  $\beta$ -gutta-percha by bands at 11.4  $\mu$ , 12.6  $\mu$ , and 13.3  $\mu$ . According to Horne et al<sup>90</sup>, a content of more than 10% trans-1,4 structures in cis-1,4 polyisoprene can be revealed by spectral differences in the range between 8  $\mu$  and 10.5  $\mu$ .

Semon et al<sup>88,99</sup> studied perdeuterio cis 1,4-polyisoprene and found an absorption band at 15.2  $\mu$  which is a =C-D  $\gamma$ -vibration and corresponds to the vibration at about 12  $\mu$  in the proteo cis-1,4 polyisoprene.

Saunders and Smith<sup>89</sup> were the first who published data on the far infrared spectra of polyisoprenes. Horne et al<sup>90</sup> showed the far infrared absorptions of natural and synthetic cis-1,4 polyisoprene. The spectra of these authors are collected in Table 7 together with our own results (see Figure 3<sup>14-17</sup>). The strongest band in all spectra occurs between 570  $\text{cm}^{-1}$  and 600  $\text{cm}^{-1}$  and is very likely a C=C-CH<sub>3</sub> bending vibration. Another fairly intense band, some 70-100 wavenumbers lower, is probably a C=C-CH<sub>2</sub> vibration, coupling with the first one. The other bands may belong to C-C-C bending vibrations.

## B. Aromatic Polyhydrocarbons (Chart II)

### 1. General Remarks on the Infrared Absorptions of Aromatic Compounds.

The infrared spectra of benzene and its derivatives have been widely studied. Useful in the structure evaluation of aromatics are bands sensitive to positions of substituents and types of substituents.



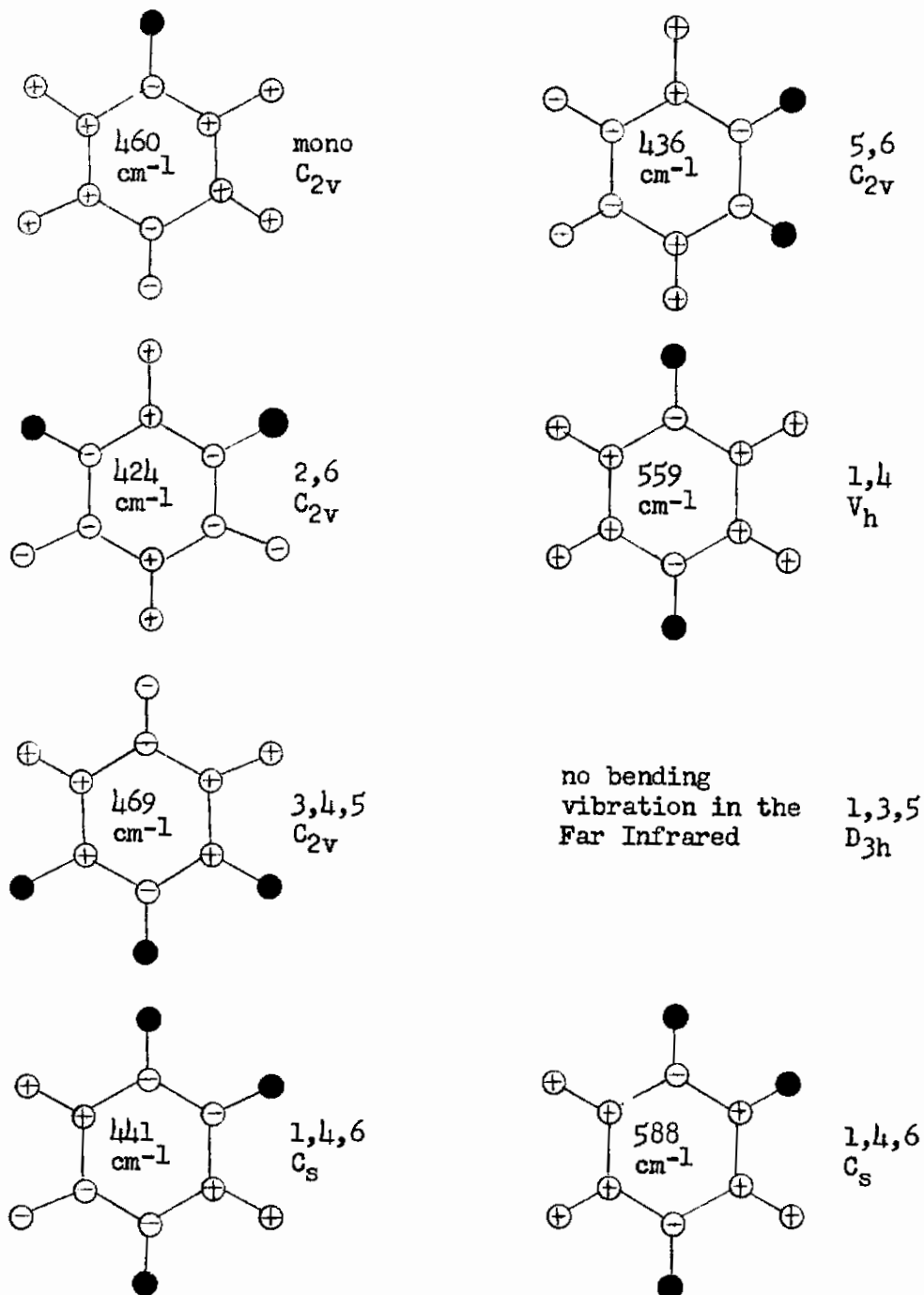
Shimanouchi et al<sup>100</sup> determined the normal coordinates for the out-of-plane C-H vibrations of benzene derivatives which proved to be sensitive to the type of substitution. Wiberley and Gonzalez<sup>101</sup> studied the infrared spectra of polynuclear aromatic compounds in the C-H stretching and out-of-plane bending regions and found valuable spectra structure correlations. Young et al found that the overtones and combination vibrations of the hydrogen out-of-plane vibrations of aromatics occurring between about 5  $\mu$  and 6  $\mu$  are characteristic for the type of substitution. Later, these bands were studied more fundamentally by Whiffen.<sup>103</sup>

Lebas<sup>104</sup> investigated the vibrational spectra of a number of mono-substituted benzene derivatives in the range between 700  $\text{cm}^{-1}$  and 200  $\text{cm}^{-1}$ . Bogomolov, in a series of papers on the vibrational spectra of aromatic compounds, published calculated and experimental data on the characteristic vibrations of meta-<sup>105</sup> and para-disubstituted<sup>106</sup> benzene derivatives. A paper by Garrigou-Lagrange et al<sup>107</sup> was also concerned with the vibrational spectra (between 1600  $\text{cm}^{-1}$  and 670  $\text{cm}^{-1}$ ) of para-disubstituted benzene derivatives. Jakobsen and Brewer<sup>108</sup> specifically discussed the spectra of para-substituted phenols in the range between 1600  $\text{cm}^{-1}$  and 300  $\text{cm}^{-1}$ . Bogomolov<sup>109</sup> discussed the characteristic vibrations of 1,2,3-substituted benzene derivatives. Jakobsen<sup>110</sup> studied the assignments of bands in the CsBr region (650  $\text{cm}^{-1}$  through 250  $\text{cm}^{-1}$ ) for a large number of aromatic compounds.

Table 8 shows the vibrational modes of out-of-plane bending vibrations below 700  $\text{cm}^{-1}$  for differently substituted benzene derivatives according to Shimanouchi et al.<sup>100</sup> For each type of substitution, the point group for the symmetry of the molecular skeleton is given. The numbers in the rings

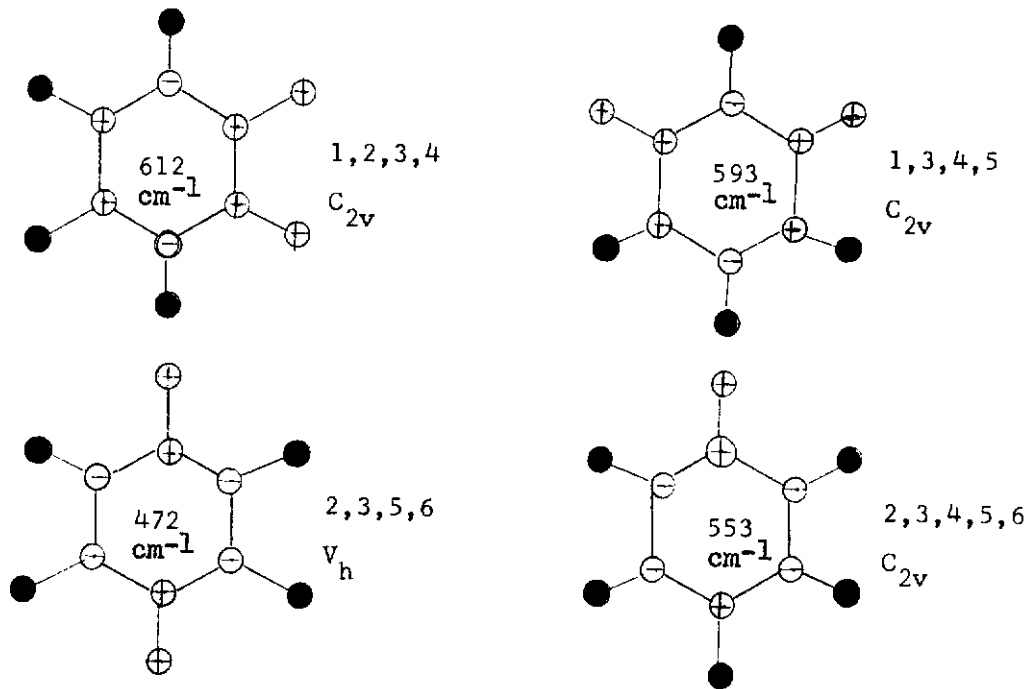
TABLE 8

Calculated Frequencies of Out-of-Plane Ring Bending Vibrations  
Below 700  $\text{cm}^{-1}$  for Different Substituted Benzene Derivatives\*



\*According to Shimanouchi et al.<sup>100</sup> The substituents are considered fixed (infinite mass).

TABLE 8 (Cont'd)



are the frequencies of the respective vibrations calculated under the assumption of infinitely heavy substituents (solid circles). The exact figures for the calculated displacement vectors are given in the original publication.

Bands of benzene derivatives in the range below about  $700\text{ cm}^{-1}$  are mainly due to bending vibrations of the aromatic system. The in-plane ring bending vibrations generally occur  $100$  to  $200\text{ cm}^{-1}$  higher than the out-of-plane ring bending vibrations. At least in the case of mono- and disubstituted benzene derivatives the out-of-plane ring deformations are more intense than the in-plane vibrations. Also, the former ones are influenced by the type of substituent (see Table 10).<sup>110</sup>

The out-of-plane bending vibrations of aromatic-bound hydrogen atoms usually occur between  $700\text{ cm}^{-1}$  and  $900\text{ cm}^{-1}$ . Only in some cases hydrogen  $\gamma$ -vibrations may be found between about  $650\text{ cm}^{-1}$  and  $700\text{ cm}^{-1}$ .

Substituents on the aromatic ring system may also show in-plane and out-of-plane bending vibrations, sometimes called  $\delta$  and  $\gamma$  vibrations, respectively. For substituents other than hydrogen, Jakobsen<sup>110</sup> gives the ranges  $220$ - $410\text{ cm}^{-1}$  (in-plane) and  $135$ - $250\text{ cm}^{-1}$  (out-of-plane) for monosubstituted benzene derivatives; and  $200$ - $460\text{ cm}^{-1}$  (in-plane) and  $140$ - $370\text{ cm}^{-1}$  (out-of-plane) for para-disubstituted benzene derivatives.

Table 9 shows the variation of the frequency of infrared-active ring deformation vibrations with the type of substitution, according to Jakobsen.<sup>110</sup> The ranges for the out-of-plane ring bending vibrations of differently substituted compounds given by Jakobsen<sup>110</sup> sometimes differ considerably from the values calculated by Shimanouchi et al.<sup>100</sup> This is probably due to the sensitivity of the out-of-plane force constants to the polarity of the



TABLE 9

Variation of Infrared-Active Ring Deformation Vibrations  
With the Type of Substitution, According to Jakobsen<sup>110</sup>

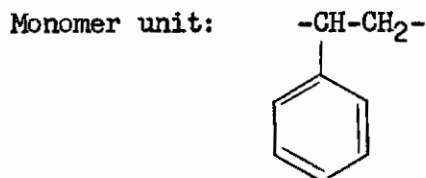
<u>Number of Substituents</u>	<u>Ring Position</u>	<u>Frequency Range</u> ( $\text{cm}^{-1}$ )	<u>Vibrational Mode (a)</u>	<u>Intensity (b)</u>
Mono-	1	605-625	$\delta$	mw-m
		418-560	$\gamma$	ms-s
Di-	1,2	495-555	$\delta$	w-m
		418-470	$\gamma$	ms-s
	1,3	505-560	$\delta$	m-ms
		415-490	$\gamma$	ms-s
	1,4	615-650	$\delta$	w-m
		446-552	$\gamma$	ms-s
Tri-	1,2,4	428-476	$\gamma$	m-s
	1,3,5	500-535	?	s
		450-470	?	m
	1,2,3	535-570	$\gamma$	s
Tetra-	1,2,3,4	568-585	?	ms-s
	1,2,3,5	505-580	$\gamma$	m-ms
	1,2,4,5	420-470	?	ms-s
Penta-	1,2,3,4,5	558-580	?	s
Hexa-	1,2,3,4,5,6	385-415	?	m-s

(a)  $\delta$ : in-plane ring deformation;  $\gamma$ : out-of-plane ring deformation

(b) w = weak, m = medium, s = strong

substituent. The effect of this sensitivity is shown in Table 10 where the positions for the out-of-plane ring bending vibration for different types of substituents are given.

## 2. Polystyrene



Conventional polystyrene is obtained by a radical process usually in a suspension or emulsion system. It is an amorphous and probably atactic polymer with no preferred configuration of the asymmetric carbon atoms in the vinyl chain.

The vibrational spectrum of polystyrene was studied by a large number of authors. The first figures on the Raman spectrum of polystyrene were given by Signer and Weiler<sup>111</sup>; a more complete Raman spectrum was published later by Palm.<sup>112</sup> Thompson and Torkington<sup>113</sup>, for the first time, discussed the infrared spectrum of polystyrene. A more thorough study of the infrared and Raman spectrum of conventional amorphous polystyrene was published by Liang and Krimm.<sup>114</sup> Their results on the far infrared absorptions, together with ours, are shown in Table 11. The approximate normal modes of the monosubstituted benzene ring in the far infrared, according to Liang and Krimm, are depicted in Table 12. Figure 18 shows the far infrared absorptions of conventional polystyrene sheets. Pfann et al<sup>115</sup> and Kammerer et al<sup>116</sup> published infrared spectroscopic methods for the determination of end groups in polystyrene.

Of the seven infrared absorptions of atactic polystyrene below  $700\text{ cm}^{-1}$ , four are in-plane and out-of-plane deformation vibrations of the aromatic

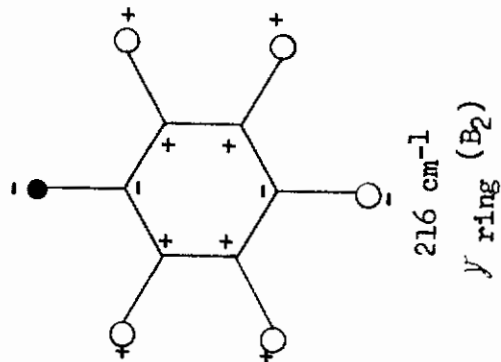
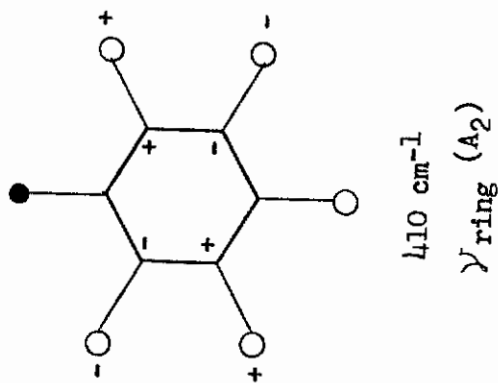
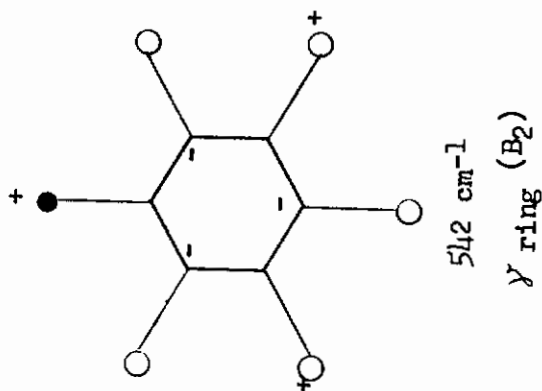
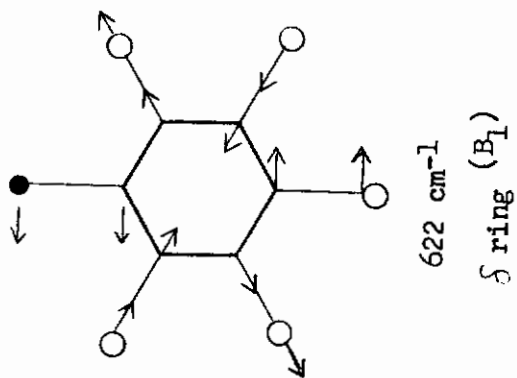
TABLE 10

Position of the Out-of-plane Ring Deformation Vibration for  
Monosubstituted Benzene Derivatives According to Jakobsen<sup>110</sup>

<u>Substituents</u>	<u>Position</u>
$\text{>C=C<}$ , $\text{-C}\equiv\text{C-}$ , $\text{-C}\equiv\text{N}$	near $550\text{ cm}^{-1}$
electron donors: $\text{-OH}$ , $\text{-NH}_2$	near $500\text{ cm}^{-1}$
electron acceptors: $\text{-COOH}$ , $\text{-NO}_2$	below $450\text{ cm}^{-1}$



TABLE 12  
 Approximate Normal Modes of Monosubstituted Benzene Ring in the Far Infrared  
 According to Liang and Krimm<sup>114</sup>



ring.<sup>114</sup> The weak bands at  $446\text{ cm}^{-1}$  and  $325\text{ cm}^{-1}$  were assigned to chain bending vibrations. The assignment of the band at about  $460\text{ cm}^{-1}$  is dubious. This band was not found by Tadokoro et al<sup>117</sup> and is not found in the spectrum of isotactic polystyrene. The assignment by Liang and Krimm<sup>114</sup> of the band at  $216\text{ cm}^{-1}$  shown in Table 12 disagrees with the calculated value of  $460\text{ cm}^{-1}$  for this vibration mode shown in Table 8. The assignments given in Table 12, therefore, may be subject to correction.

Isotactic polystyrene was first described by Natta and Corradini.<sup>118</sup> It is formed during the polymerization of styrene by stereospecific catalysts of the Ziegler type and can be isolated from the crude polymer as an ether-insoluble matter. It is highly crystalline, has a molecular weight of  $10^5$ - $10^6$ , and a first order transition temperature of about  $210^\circ\text{C}$ . The X-ray density of the crystallites is 1.124. The unit cell is similar to that of isotactic polypropylene. It contains two chain sequences parallel to the chain axes with three monomer units per repeat. The conformation of the chains is helical with three monomer units in a coil as in the helix of isotactic polypropylene. A crystallizable polystyrene, prepared by "Alfin" catalysts, is probably also isotactic<sup>119,120</sup>. The infrared spectrum of isotactic polystyrene (see figure 19) was studied by a large number of authors.<sup>117,119-128</sup> The spectra of deuterated isotactic and atactic polystyrenes were also studied<sup>117,123,125,127</sup>. The spectrum of isotactic, crystalline or amorphous, polystyrene is distinctly different from the spectrum of atactic polystyrene.

Tadokoro et al<sup>117,122</sup> were the first who could show that bands in the crystalline material at  $1363$ ,  $1314$ ,  $1297$ , and  $1185\text{ cm}^{-1}$  ( $7.33$ ,  $7.61$ ,  $7.71$ , and  $8.44\ \mu$ ) belong to  $\text{CH}_2$  and  $\text{CH}$ -wagging and twisting vibrations, and very likely are connected with the helical conformation of the chains. This assignment is supported by the observation that similar bands at  $1358$ ,  $1304$ , and

# Contraails

1167  $\text{cm}^{-1}$  are found in the spectrum of crystalline, isotactic polypropylene. The strongest evidence for this assignment is given by the fact that similar bands can be observed also in the spectra of isotactic and ring-substituted (methyl, deuterium) polystyrenes, but not in chain-deuterated isotactic polystyrenes <sup>117,122,129</sup>. Since in the case of quenched isotactic polystyrene these bands are weaker but still observable, it is concluded that amorphous isotactic polystyrene at least partially retains the helical structure. Also, these bands remain in the spectrum of dissolved ( $\text{CS}_2$ ) isotactic polystyrene. Hence, it is reasonable to assume that the helices essentially remain intact also in solution.\* (As to the discussion of three different types of bands sensitive to changes in configuration, conformation, and crystallinity, see also Takeda et al, <sup>119,120</sup> and Onishi and Krimm. <sup>127</sup>

A second group of bands, including five in the far infrared range, do not occur in the spectrum of atactic polystyrene. However, they can be observed only in crystalline isotactic polystyrene and disappear upon melting or dissolving of the material. They are very likely connected with far reaching intra and intermolecular interactions in the crystalline material. The maxima of the bands are at 984, 923, 901, 620, 587, 499, 465, and 426  $\text{cm}^{-1}$  (10.16, 10.83, 11.10, 16.13, 17.04, 20.04, 21.5, and 23.5  $\mu$ ). Especially useful for the determination of crystallinity are the bands at 984  $\text{cm}^{-1}$  and 499  $\text{cm}^{-1}$ . <sup>121,128</sup>

The doublet at 1085  $\text{cm}^{-1}$  and 1054  $\text{cm}^{-1}$  as well as the asymmetric band at 567  $\text{cm}^{-1}$  are vibrations of the phenyl group and form a third group of bands. <sup>119,120</sup> They are sensitive against the short-range order within a chain, i.e., the alternating trans-gauche conformation in the isotactic

\*This can probably not be generalized. Schmidt<sup>55</sup> for instance concluded from his experimental results that amorphous isotactic polypropylene has a non-helical conformation.

sequences, and all-trans conformation in syndiotactic sequences. The band at about  $565\text{ cm}^{-1}$  (the figures given for this band slightly differ in the different papers) is very likely characteristic for trans-gauche sequences. Takeda et al<sup>120</sup> suggest the ratio of the absorbances  $A_{560}/A_{543}$  as a measure for isotactic sequences.

The observation of this group of bands characteristic for short range order in stereoregular polymers is of basic interest since one and three-dimensional crystallinity are derived magnitudes, and consequently not in all instances a measure of the content of a polymer in eutectic configurations.

### 3. Copolymers of Styrene.

"Zerlon 150" is a copolymer of about equal parts of styrene with methyl methacrylate. In its far infrared spectrum (Figure 20), the bands of both monomer units can be observed. However, the intense doublet of polystyrene near  $540\text{ cm}^{-1}$  is fused to a single band with its maximum at  $550\text{ cm}^{-1}$ .

### 4. Poly- $\alpha$ -methylstyrene

Bentley and Wolfarth,<sup>19</sup> in their publication on the analytical applications of far infrared spectra, studied a number of alkylsubstituted benzene derivatives. From their spectra of monosubstituted alkylbenzenes, it is evident that the strong band in the range of about  $18\text{-}21.5\ \mu$  ( $555\text{-}465\text{ cm}^{-1}$ ) is very sensitive to  $\alpha$ -branching of the substituent. Normal alkylbenzenes and iso-alkylbenzenes with the branching not in  $\alpha$ -position show this band around  $500\text{ cm}^{-1}$ . A branching in  $\alpha$ -position shifts this band to about  $550\text{ cm}^{-1}$  whereas a second branch in  $\alpha$ -position apparently has only a slight influence on the position of this band. The values for iso-butylbenzene, sec-butylbenzene, and tert-butylbenzene are  $496\text{ cm}^{-1}$ ,  $543$  and  $537\text{ cm}^{-1}$  (doublet) and  $544\text{ cm}^{-1}$ , respectively.



The same observation can be made with polystyrene and poly- $\alpha$ -methylstyrene. The former absorbs at  $536\text{ cm}^{-1}$  (Figure 18), the latter at  $547\text{ cm}^{-1}$  (Figure 21). However, the band of polystyrene is, as in the case of isobutylbenzene, an unresolved doublet, whereas the band of poly- $\alpha$ -methylstyrene is a single, almost symmetrical band as in the spectrum of tert-butylbenzene.

In this connection, it has to be mentioned that Jakobsen<sup>110</sup> assigns a band near  $540\text{ cm}^{-1}$  in the spectra of alkylbenzenes to a C-C-C bending vibration of the substituent, whereas Liang and Krimm<sup>114</sup> assigned this band in polystyrene to an out-of-plane ring bending vibration (see Table 12).

## 5. Ring-Substituted Polystyrenes

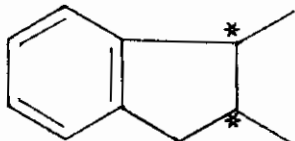
Ring-substituted styrenes, as styrene itself, can be polymerized with stereospecific catalysts. The resulting polymers are amorphous and crystallize only with difficulty.<sup>129</sup> However, they have an isotactic and helical structure similar to that of isotactic polystyrene. This is evidenced by the appearance of bands assigned to the helical vinyl chain,  $1361$ ,  $1314$ , and  $1290\text{ cm}^{-1}$  for poly-p-methylstyrene, and  $1361$ ,  $1310$ , and  $1190\text{ cm}^{-1}$  for poly-m-methylstyrene.<sup>122</sup> Another support for the isotactic and helical structure of these ring-substituted polystyrenes, prepared with Ziegler catalysts, is the observation of Natta et al<sup>126</sup> that isotactic polystyrene and poly-p-methylstyrene are isomorphous. The far infrared spectra of these polymers are not published as yet.

The atactic ring-substituted derivatives of polystyrene have had industrial interest. The strongest band in the far infrared spectrum of atactic poly-p-methylstyrene (Figure 22) is a doublet with maxima at about  $553\text{ cm}^{-1}$  and  $530\text{ cm}^{-1}$ . The position of the former agrees well with the frequency calculated for an out-of-plane bending vibration of 1,4-substituted

benzene derivatives of the point group  $V_h$  by Shimanouchi et al<sup>100</sup> (Table 8). In the far infrared spectrum of poly-p-isopropylstyrene (Figure 23), the maximum of this band is shifted to about  $580 \text{ cm}^{-1}$ . A technical copolymer of vinyl toluene (mixture of isomers) and acrylonitrile was Cymac 201 (Figure 24).

## 6. Polyindene

The olefinic double bond of indene is fairly reactive. Hence, indene can be polymerized with Lewis and other acids. Polyindenenes of technical grade are resins with a rather low molecular weight; they are used as chemically resistant components in surface coatings. The monomer unit in

polyindenenes  contains two different asymmetric carbon atoms. Furthermore, the addition may happen in head-to-tail or head-to-head and tail-to-tail fashion. Consequently, a number of different stereoregular polymers is theoretically possible. To date, nothing has been published about stereoregular polyindenenes.

The far infrared spectrum of a technical polyindene (Figure 25) is characterized by a fairly strong band at about  $420 \text{ cm}^{-1}$ . This agrees rather well with the value ( $436 \text{ cm}^{-1}$ ) calculated by Shimanouchi et al<sup>100</sup> for an out-of-plane bending vibration of o-substituted benzene derivatives (see Table 8).

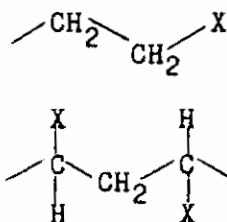
## C. Halogenated Polyhydrocarbons (Chart III)

### 1. Chlorinated Polyhydrocarbons.

It has been generally observed that certain vibrations in a molecule are sensitive to the conformation of the vibrational group with respect to a neighboring group. Thus, the C-X stretching vibration in l-substituted alkanes

is sensitive to the position of the substituent X with respect to the C-atom in  $\beta$  position. In vinyl polymers of the general formula  $(-\text{CH}-\text{CH}_2)_n$ , the C-X stretching vibration

is sensitive to the conformation of the C-C chain.



The carbon-halogen stretching vibrations in alkyl halides should receive consideration since they are easily detectable and rather sensitive to the conformation in the chain.<sup>130-137</sup> According to Brown and Sheppard<sup>135</sup>, the 1,2-dihalogen ethanes have two spectroscopically distinguishable rotational isomers, namely, a trans-form where the two halogens are in a trans-position, and a gauche form where the two halogens are at an angle of  $60^\circ$  to each other with respect to the C-C bond. Trimethylene halides have four spectroscopically distinguishable rotational isomers, namely, those in trans-trans, trans-gauche, and in two different gauche-gauche conformations. As the methylene chain between the chlorine atoms becomes large, the number of possible rotational isomers increases. However, these isomers finally become indistinguishable by infrared spectroscopic methods.

Shimanouchi and his coworkers<sup>136,137</sup> proposed a rule concerning the spectral regions of various C-Cl stretching vibrations. According to this, the C-Cl stretching band of secondary chlorides with Cl trans to H is expected between  $600 \text{ cm}^{-1}$  and  $640 \text{ cm}^{-1}$ ; the C-Cl stretching band with Cl trans to C is expected between  $670 \text{ cm}^{-1}$  and  $700 \text{ cm}^{-1}$ .

These considerations can be transferred to vinyl polymers, especially to the polyvinyl halides and similar compounds. However, every second carbon atom in polyvinyl halides is asymmetric, and the configuration of the substituents at these carbon atoms may be either d or l. The possible chain

conformations in polyvinyl halides therefore depend on the configuration at the asymmetric carbon atoms. This shall be discussed for polyvinyl chlorides of a different structure.

a. Polyvinyl Chloride. Conventional polyvinyl chloride is obtained by an emulsion or dispersion polymerization and with radical catalysts. Dehalogenation with metallic zinc yields a polymer with cyclopropane groups<sup>138,139</sup>; this is chemical proof for the head-to-tail structure of polyvinyl chloride. Conventional polyvinyl chloride is not crystallizable. The asymmetric carbon atoms in its vinyl chain seem to have a somewhat prevailing d,l configuration according to a syndiotactic chain. However, this problem is not settled definitively.

The infrared spectrum of polyvinyl chloride was studied by a large number of authors.<sup>137,140-159</sup> The most comprehensive discussion of its spectrum between  $3200\text{ cm}^{-1}$  and  $100\text{ cm}^{-1}$  was given by Krimm<sup>3</sup> and Liang.<sup>145</sup> Stromberg et al<sup>160</sup> observed band shifts in the spectrum of thermally degraded polyvinyl chloride.

Polymerization at low temperatures seems to favor the formation of syndiotactic chains.<sup>148</sup> There are also some catalyst systems with a certain degree of stereospecificity which preferably form syndiotactic and crystallizable polyvinyl chloride. Kawasaki et al<sup>156</sup> used a mixture of aluminum triethyl and di-tert-butylperoxide at room temperature, and a mixture of boron triethyl and cumene hydroperoxide at  $-65^{\circ}\text{C}$ . Takeda and Iimura<sup>159</sup> used a mixture of boron triisobutyl and azo-diisobutyronitrile as a catalyst. The radiation-initiated polymerization of vinyl chloride-urea complexes at low temperatures also yields crystallizable polymers with a high degree of syndiotacticity.<sup>137,147,152</sup>

# Contrails

Samples with different density, and probably also with different crystallinity, were studied by Kawasaki et al.<sup>150,156</sup> The authors found absorptions increasing with the density of a sample at 1428, 1333, 1254, 1226, and 961  $\text{cm}^{-1}$  (7.00, 7.50, 7.98, 8.15, and 10.41  $\mu$ ).

The assignment of the four C-Cl stretching vibrations\* in the far infrared (690, 638, 615, and 603  $\text{cm}^{-1}$ ) for some time was a subject of controversy between different groups of spectroscopists. The first, and probably most complex absorption (680-690  $\text{cm}^{-1}$ ) is in the range for conformations with Cl trans to C; the three others are in the range for conformations with Cl trans to H. These conformations are possible for certain structures in both isotactic and syndiotactic sequences. Table 13 lists assignments for polyvinyl chloride. These assignments are based on experimental results of Krimm et al.<sup>147</sup> with highly syndiotactic and crystalline material which does not show the band at 680-690  $\text{cm}^{-1}$  and on data observed by Shimanouchi et al.<sup>137,157</sup>

Extremely interesting are the studies of Shimanouchi and Tasumi<sup>157</sup> with stereoregular 2,4-dichloropentanes. Table 14 shows the possible rotational isomers of meso and dl-2,4-dichloropentanes. Applying the rule of Shimanouchi et al.<sup>136,137</sup>, we can expect two bands in the range 600-640  $\text{cm}^{-1}$  (Cl trans to H) for structure I, two bands between 670  $\text{cm}^{-1}$  and 700  $\text{cm}^{-1}$  (Cl trans to C) for structure II, and one band in each of the two ranges for structure III (in structure III one Cl is trans to H and one Cl trans to C). Table 15 shows the far infrared absorptions of the different 2,4-dichloropentanes. Apparently the dl-form has the structure I and the meso form, the structure III.

\*It is noteworthy that these four bands are to some extent sensitive to deuteration of the chain. They are, therefore, not pure C-Cl stretching vibrations but couple with chain vibrations.

TABLE 13

Far Infrared Bands of Polyvinyl Chloride\*

<u>Wavenumber, cm<sup>-1</sup></u>	<u>Dichroic Behavior</u>	<u>Assignment</u>
690 680)unresolved		$\nu(\text{C-Cl})$ ; Cl trans to C, isotactic sequences
638	⊥	$\nu(\text{C-Cl})_{oi}(\text{B}_{1u})^{**}$ in cryst. regions
615	⊥	$\nu(\text{C-Cl})$ in amorphous regions
603	⊥***	$\nu(\text{C-Cl})_{io}(\text{B}_{2u})^{**}$ in cryst. regions
540	?	Combination vibration
487	⊥	$\nu(\pi/2)_o(\text{B}_{1u})^{**}$
430	⊥	$\delta(\text{C-Cl})_{oi}(\text{B}_{1u})^{**}$
363	Not determined	$\delta(\text{C-Cl})_{io}(\text{B}_{2u})^{**}$
315	Not determined	$\gamma_w(\text{C-Cl})_{oi}(\text{B}_{3u})^{**}$
182	Not determined	$\nu(\pi/2)(b_2)_i(\text{B}_{3u})^{**}$
160	Not determined	$\nu(\pi/2)(a_1)_o(\text{B}_{2u})^{**}$
102	Not determined	$R'_o(\text{B}_{1u})$ (rotation)

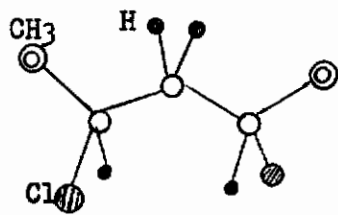
\*Selected from the results of several authors.

\*\*Assignments according to Krimm.<sup>3</sup> The subscripts refer to in-phase (i) and out-of-phase (o) motions, the first subscript referring to the value of the mode in a single chain, and the second subscript to the relationship between the motions of the two chains in the unit cell.

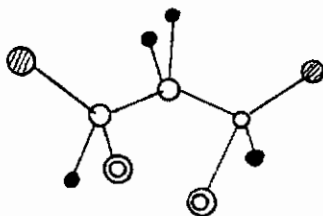
\*\*\*Inversion of dichroism with drawing.<sup>158</sup>

TABLE II

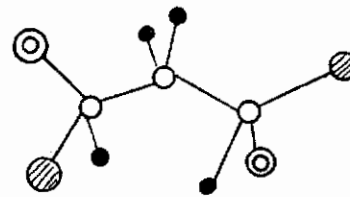
Possible Rotational Isomers of Meso and dl-2:4-Dichloropentanes  
According to Shimanouchi and Tasumi<sup>157</sup>



Structure I\*  
(dl-form)



Structure II\*  
(dl-form)



Structure III\*\*  
(meso-form)

\*Model compound for syndiotactic polyvinyl chloride.

\*\*Model compound for isotactic polyvinyl chloride.

TABLE 15

## Far Infrared Absorptions of 2:4-Dichloropentanes

<u>Compound</u>	<u>Phase</u>	<u>Wavenumber, cm<sup>-1</sup></u>	
dl-2:4-dichloropentane	Gaseous	645	622
	Liquid	631	610
	Solid	623	597
meso-2:4-dichloropentane	Liquid	683	619



# Contrails

In fact, dl-2,4-dichloropentane is a model compound for syndiotactic polyvinyl chloride and meso 2,4-dichloropentane is a model compound for isotactic polyvinyl chloride. The two C-Cl bands observed in the spectrum of dl 2,4-dichloropentane correspond exactly to the bands at  $638\text{ cm}^{-1}$  and  $603\text{ cm}^{-1}$  found in crystalline, syndiotactic polyvinyl chloride. The only possible structure for a chain of this type with Cl trans to H is an extended syndiotactic one.

The band at  $690\text{ cm}^{-1}$  belongs to a conformation Cl trans to C. The dl-2,4-dichloropentane showed no band near  $690\text{ cm}^{-1}$  but the meso form did. Consequently, it is very likely that the band near  $690\text{ cm}^{-1}$  in conventional polyvinyl chloride belongs to isotactic sequences, probably in a helical conformation. The possible conformations in conventional polyvinyl chloride are shown in Table 16.

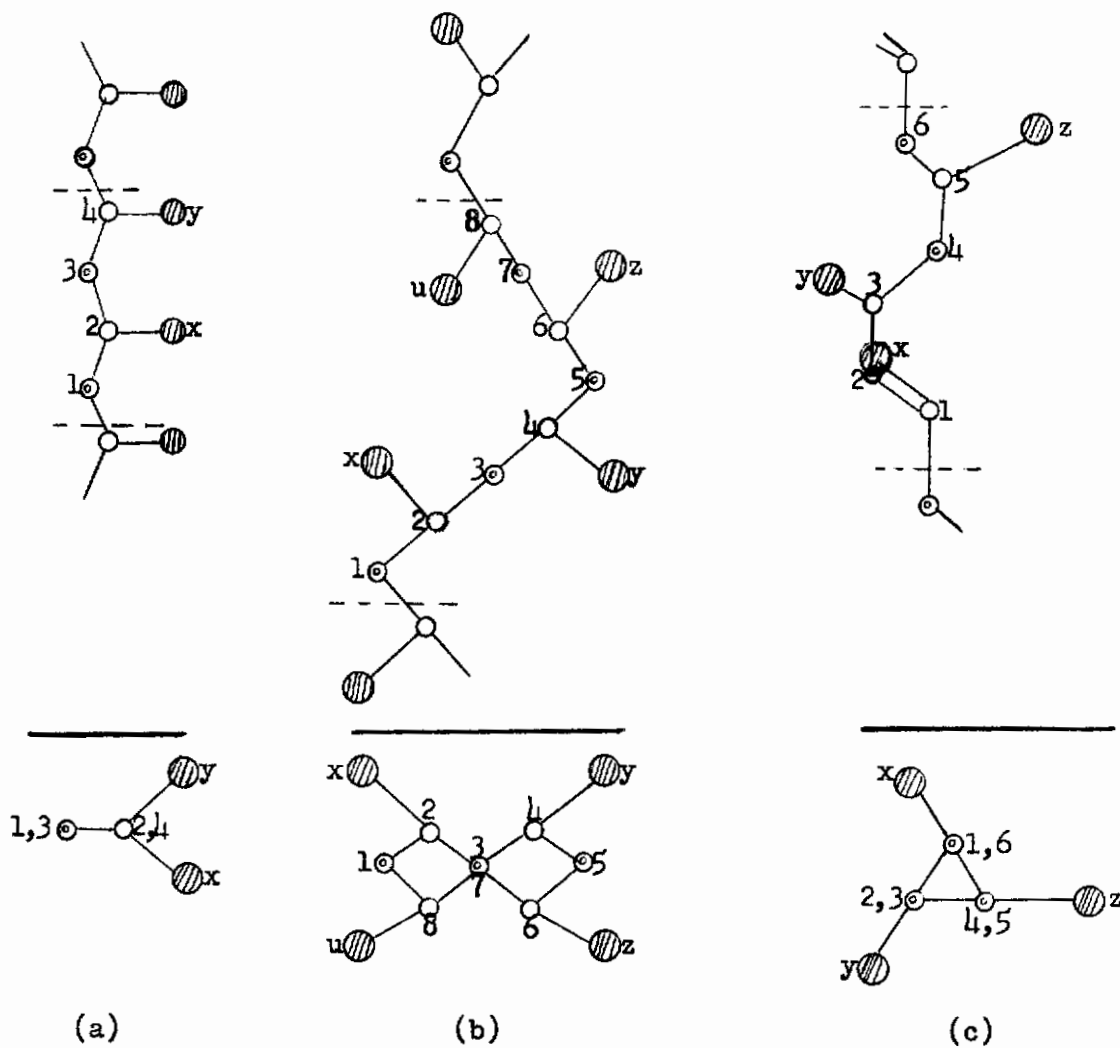
Figure 26 shows the absorptions of a sheet of conventional polyvinyl chloride. The bands at  $615\text{ cm}^{-1}$  and  $603\text{ cm}^{-1}$  cannot be resolved without the application of polarized infrared.

Vinylchloride-vinylacetate copolymers are widely used in coatings and cements. The content in vinylacetate units makes the polymers more soluble in the usual solvents for lacquers. The far infrared spectrum of a copolymer with about 15% vinylacetate (Figure 27) is very similar to that of a pure polyvinyl chloride. This is mainly due to the fact that the strongest band of polyvinyl acetate near  $605\text{ cm}^{-1}$  is masked by the much stronger band of polyvinyl chloride near  $615\text{ cm}^{-1}$ . Copolymers of this type, however, can readily be identified by their infrared spectrum in the rocksalt range.

b. Polyvinylidene Chloride. Vinylidene chloride polymerizes with radical catalysts to yield a polymer which is not readily soluble in most of

TABLE 16

Possible Formations of Polymer Chains in Conventional  
Polyvinylchloride\*



- (a) extended syndiotactic structure (all trans; likely)
- (b) folded syndiotactic structure (-trans-trans-gauche-gauche-; unlikely)
- (c) threefold isotactic helix (-trans-gauche-trans-gauche-; likely)

\*T. Shimanouchi and M. Tasumi, Spectrochim. Acta 17, 755-60 (1961)

the conventional solvents. For industrial use, it is therefore copolymerized with about 15% vinyl chloride. These copolymers, known as "Saran" (Figure 28) or "Krehalon," are readily soluble in a number of solvents. The anionic polymerization and copolymerization of vinylidene chloride was described by Konishi<sup>161</sup> (more literature is given in this publication).

The identity period of the chain axis, according to X-ray examination, is rather short, namely 4.7 Å. This is more than one monomer unit but less than two for a planar zigzag. Two possible structures were suggested for this repeating period, both containing two monomer units, one by Fuller<sup>162</sup>, the other by Reinhardt.<sup>163</sup> In both structures the carbon skeleton is folded.

The infrared spectra of polyvinylidene chloride and, preferably, vinylidene chloride-vinyl chloride copolymers were studied by a number of authors.<sup>140,164-167</sup> Table 17 shows the far infrared absorptions of a vinylidene chloride-vinyl chloride copolymer with a low content of vinyl chloride. The only absorptions observable, and belonging to the vinyl chloride units or to the copolymer, are the bands at 1206  $\text{cm}^{-1}$  and 868  $\text{cm}^{-1}$  (8.29  $\mu$  and 11.52  $\mu$ ). A weak band found by Krimm and Liang<sup>164</sup> near 307  $\text{cm}^{-1}$  was not observed in our spectrum.

The assignment of the bands at 754, 657, 603, and 530  $\text{cm}^{-1}$  to  $\text{CCl}_2$  stretching modes, supported by deuteration studies\*, and their dichroic behavior is essential to the choice of the correct structure. Due to the two monomer units in the repeating unit and the phase relations between them, the fundamental vibrations of the  $\text{CCl}_2$  group are doubled. As Krimm and Liang pointed out, two rather strong perpendicular bands, a weaker parallel band, and an almost inactive band should be characteristic for the Reinhardt<sup>163</sup>

\*As in the case of polyvinyl chloride, the  $\text{CCl}$  stretching vibrations couple quite considerably with skeleton vibrations.

TABLE 17

Far Infrared Absorptions of Polyvinylidene Chloride

<u>Krimm and Liang<sup>164</sup></u> (Copolymer with a small amount of Vinyl Chloride) <u>Wavenumber, cm<sup>-1</sup></u>	<u>This Report</u> (Dow Saran) <u>Wavenumber, cm<sup>-1</sup></u>	<u>Dichroic</u> <u>Behavior*</u>	<u>Assignment*</u>
754	749	⊥	$\gamma_a(\text{CCl}_2)_o$ (A')
657	654	⊥	$\gamma_a(\text{CCl}_2)_i$ (A')
603	598	⊥	$\gamma_s(\text{CCl}_2)_o$ (A')
565	563-555		?
530	528	⊥	$\gamma_s(\text{CCl}_2)_i$ (A')
454	449		$\gamma_t(\text{CCl}_2)_i$ (A'') ?; skeletal ?
430	430		$\gamma_t(\text{CCl}_2)_o$ (A'') ?; skeletal ?
359	354		$\gamma_w(\text{CCl}_2)_i$ (A'')
307	-	---	$\gamma_r(\text{CCl}_2)_o$ (A')
291	approx. 280	---	$\gamma_r(\text{CCl}_2)_i$ (A')
245	-	---	$\delta(\text{CCl}_2)_i$ (A')
185	-	---	skeletal ?
113	-	---	skeletal ?
102	-	---	skeletal ?

\*According to Krimm and Liang<sup>164</sup>

structure. On the other hand, the Fuller<sup>162</sup> structure implies four perpendicular bands, two of them stronger than the other two. The experimental results strongly support the Fuller<sup>162</sup> structure.

Polyvinylidene chloride is crystallizable. According to Narita et al<sup>166</sup>, the bands at 884, 753, 655, 600, 565, 527, and 450  $\text{cm}^{-1}$  are much weaker in molten samples. Actually, the long wavelength vibrations almost fuse together into a very broad and poorly structured band. This indicates a basic change in the structure of the polymer during melting.

Quenched samples recrystallize slowly at room temperature. This can be followed by changes in the far infrared spectrum. Stretching speeds up the rate of recrystallization.

c. Other Chlorinated Polyhydrocarbons. Enjay Chlorobutyl is a low-chlorinated butyl rubber. The bands in its far infrared spectrum (Figure 29) are weak; the one near 670  $\text{cm}^{-1}$  may be a C-Cl stretching vibration. The spectrum as a whole differs little from the spectrum of butyl rubber.

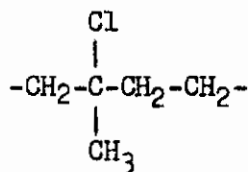
Chlorinated and chlorosulfonated polyethylenes obtained considerable industrial interest as components in surface coating and synthetic rubbers. Canterino and Kahle<sup>168</sup> recently published a rather thorough study on the properties of chlorinated and chlorosulfonated high- and low-density polyethylenes and ethylene- $\alpha$ -olefin copolymers.

The far infrared spectrum of a chlorinated high-pressure (low-density) polyethylene (Figure 30) shows rather strong bands near 660  $\text{cm}^{-1}$  and 610  $\text{cm}^{-1}$ . Both must be C-Cl stretching vibrations for groups with different conformation. The latter band belongs to conformations with Cl trans to H, the former probably to conformations Cl trans to C.

# Contrails

The infrared spectrum of chlorosulfonated polyethylene was described by Smook et al.<sup>169</sup> Its far infrared spectrum (Figure 31) has the same C-Cl bands as chlorinated polyethylene. Additional bands near 590, 565, and 533  $\text{cm}^{-1}$  can possibly be connected with the  $\text{SO}_2\text{Cl}$  groups. This spectral behavior is consistent with the structure. Chlorosulfonated polyethylene contains 26 - 29 percent chlorine and only 1.3 - 1.7 percent sulfur. Consequently, the chlorine in its major part is bound directly to the chain as in chlorinated polyethylene.

The compound, 1,4-polyisoprene, adds hydrogen chloride to its olefinic double bonds; according to Markovnikov's rule, the chlorine is added to the carbon atom with the smaller number of hydrogen atoms:



Checkland and Davison<sup>170</sup> described the infrared spectrum of hydrochlorinated Hevea rubber. Its far infrared spectrum (Figure 32) shows some similarity to the spectrum of conventional polyvinyl chloride (Figure 26). Bands at 743  $\text{cm}^{-1}$  and 640  $\text{cm}^{-1}$  were assigned to C-Cl stretching vibrations of groups where Cl is trans or gauche to the  $\text{CH}_2$  group.<sup>170</sup>

The chlorination of Hevea rubber not only leads to an addition of chlorine to the olefinic double bond but also to substitution reactions. The infrared spectrum of chlorinated rubber was studied by a number of authors.<sup>171-174</sup> Its far infrared spectrum (Figure 23) differs significantly from that of hydrochlorinated rubber or polyvinyl chloride. Due to the irregular structure of chlorinated rubber and the many possible conformations of the chain, comments on the far infrared spectrum were not attempted.

# Contrails

The infrared spectrum of after-chlorinated polyvinyl chloride was studied by Fuchs and Louis.<sup>175</sup> No figures were available for the far infrared region.

## 2. Fluorinated Polyhydrocarbons, Polyfluorocarbons, and Poly(chlorofluorocarbons)

a. Polyvinyl Fluoride. Vinylfluoride polymerizes with radical catalysts at high pressures to form a polymer with a melting range of 170-190°C and a density of 1.30 g cm<sup>-3</sup>. A polymerization process was described by Kalb et al.<sup>176</sup> Polyvinyl fluoride ("Teslar") is used for chemically resistant surface coatings and for films.

The strong bands in its far infrared spectrum (Figure 34) are mainly due to deformation vibrations involving the CHF group. Since they are weaker than the extremely strong CF-stretching vibrations in the range of 1100 cm<sup>-1</sup>, the conventional films with thicknesses around 50 μ can easily be studied in the far infrared but not in the rocksalt range.

b. Polyvinylidene Fluoride. Vinylidene fluoride can be polymerized with radical catalysts. (See McBee et al.<sup>177</sup>) The polymers melt around 170°C and have a density of 1.76 g cm<sup>-3</sup>. The technical product is called "Kynar."

The far infrared absorptions of polyvinylidene fluoride (Figure 35) mainly stem from deformation vibrations of the CF<sub>2</sub> group. As already mentioned for polyvinyl fluoride, the stretching vibrations in the rocksalt range are extremely strong. Hence the far infrared range is more suitable for the identification of films with the usual thicknesses around 50 μ.

c. Polytetrafluoroethylene. Polytetrafluoroethylene is a highly crystalline material with a density of 2.2 g/cc and a transition temperature

# Conclusions

of 327°C. However, the material does not really melt at this temperature but only becomes amorphous and plastic.

According to X-ray studies of Bunn and Howells<sup>178</sup>, a polymer chain in crystalline polytetrafluoroethylene consists of a helical arrangement of 13 CF<sub>2</sub> groups in the identity period. There is a phase transition at 19°C which seems to be accompanied by a change in the identity period, there now being 15 CF<sub>2</sub> groups in the repeat.<sup>179</sup>

The infrared spectrum of the polymer was investigated by a number of authors.<sup>180-186</sup> The far infrared bands and their assignments given by Krimm<sup>3</sup>, together with those found through this study, are shown in Table 18. It is interesting to note the parallelism between the infrared spectra of polyethylene (Figure 3) with the structure (CH<sub>2</sub>-)<sub>n</sub>, and that of polytetrafluoroethylene with the structure (CF<sub>2</sub>-)<sub>n</sub> (Figure 36). However, the CF<sub>2</sub>-bending vibration has a lower frequency than the CF<sub>2</sub>-wagging frequency. Generally, the intramolecular forces in the (CF<sub>2</sub>-)<sub>n</sub> chain are much stronger than in the polyethylene chain. This is also expressed by the fact that a minor change in the structure, namely the rearrangement of the thirteen-fold helix to a fifteen-fold helix, can be noticed by a shift of the CF<sub>2</sub>-wagging vibration from 638 cm<sup>-1</sup> to 625 cm<sup>-1</sup>. In cases of weaker intra- or intermolecular forces, enantiomorphous modifications may have the same infrared spectrum.

Infrared methods for the determination of crystallinity in polytetrafluoroethylene were described by Pokrovsky and Kotova<sup>184</sup>, and by Miller and Willis.<sup>186</sup> A method for the determination of end groups in polytetrafluoroethylene was described by Bro and Sperati.<sup>182</sup>



TABLE 18

Far Infrared Absorptions of Polytetrafluoroethylene

<u>Krimm<sup>3</sup></u>	<u>This Report</u>	<u>Dichroic Behavior</u>	<u>Assignment<sup>1</sup></u>
<u>Wavenumber, cm<sup>-1</sup></u>			
740	738		Not determined
720	717		Not determined
703	700 (sh)**	Not determined	Not determined
-	670 (sh)**	Not determined	Not determined
638	638		$\gamma_w(\text{CF}_2)$ ( $A_2$ ) <sub>13</sub>
625	625		$\gamma_w(\text{CF}_2)$ ( $A_2$ ) <sub>15</sub>
553	554	⊥	$\delta(\text{CF}_2)$ ( $E_1$ )
516	515		$\gamma_r(\text{CF}_2)$ ( $A_2$ )
384	380-385		Not determined
321	*	Not determined	$\gamma_t(\text{CF}_2)$ ( $E_1$ )
277	*	Not determined	$\gamma_w(\text{CF}_2)$ ( $E_1$ )
203	-		$\gamma_r(\text{CF}_2)$ ( $E_1$ )
149	-	Not determined	Not determined
124	-	Not determined	Not determined
102	-	Not determined	Not determined

\*Not observed due to strong water bands  
 \*\*sh = shoulder

d. Polychlorotrifluoroethylene. Polychlorotrifluoroethylene is highly crystalline and differs from polytetrafluoroethylene by melting at about 300°C without decomposition. Its structure is not yet fully understood. It is assumed that it is stereoregular and has a helical structure.

The infrared spectrum of the polymer was studied by Liang and Krimm.<sup>180</sup> Their figures and assignments, together with ours (Figure 37), are shown in Table 19. Iwasaki et al<sup>187</sup> studied the decomposition of polychlorotrifluoroethylene by an infrared spectroscopic method. Hoffman and Weeks<sup>188</sup> and Matsuo<sup>189,190</sup> determined the crystallinity of the polymer by an infrared method.

Iwasaki et al<sup>191</sup> studied the infrared spectra of tetrafluoroethylene-trifluorochloroethylene copolymers. They found characteristic bands for different arrangements between the tetrafluoroethylene (A) and trifluorochloroethylene (B) monomer units: ABA 957  $\text{cm}^{-1}$ , ABB 967  $\text{cm}^{-1}$ , BBB 971  $\text{cm}^{-1}$ .

A copolymer of chlorotrifluoroethylene and vinylidene fluoride (KEL-F 827) has a far infrared spectrum (Figure 37) very similar to that of pure polytrifluorochloroethylene (Figure 38). Only the shift of the maximum at 500  $\text{cm}^{-1}$  to 510  $\text{cm}^{-1}$  reveals the presence of the vinylidene fluoride unit.

## D. Alkyds and Other Resinous Esters (Chart IV)

### 1. General Remarks on the Far Infrared Absorptions of Esters.

If we consider the ester group as a plane, three-pointed star, then this "molecule" of four atoms is able to perform the following vibrations:

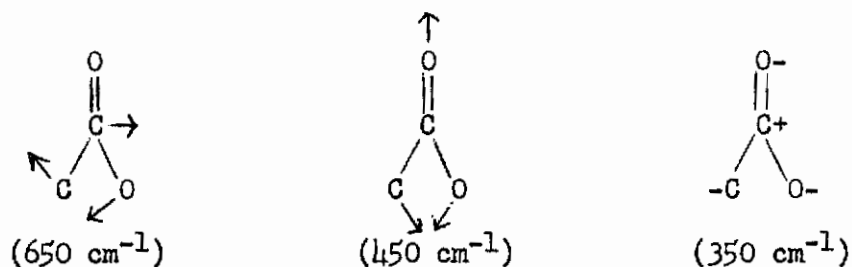
TABLE 19

Far Infrared Absorptions of Polychlorotrifluoroethylene

<u>Liang and Krimm<sup>180</sup></u>	<u>This Report</u>	<u>Dichroic Behavior</u>	<u>Assignment<sup>180</sup></u>
<u>Wavenumber, cm<sup>-1</sup></u>			
-	689	Not determined	-
658	666		-
580	589		CF <sub>2</sub> wagging (A)
(535)	530(sh)*	?	-
506	501	⊥?	CF <sub>2</sub> bending (E <sub>1</sub> )
490	?		CF <sub>2</sub> rocking (A)
438	436		CCLF wagging (A)
390	385	?	-
365	-	?	-
335	330-35	unpol.	CCLF bending (E <sub>1</sub> )
297	-	Not determined	CF <sub>2</sub> wagging (?) (E <sub>1</sub> )
235	-	Not determined	CF <sub>2</sub> rocking (E <sub>1</sub> )
185	-	Not determined	CCLF rocking (E <sub>1</sub> )
102	-	Not determined	-

\*sh = shoulder

# Contrails



The first one is asymmetric with respect to the C=O axis and a degenerate vibration. During this vibration all atoms of the group perform nonlinear movements in the plane of the ester group. In a first approximation, the single-bonded C and O describe circles. The second one is a bending vibration symmetric to the C=O axis, the third one is an out-of-plane deformation vibration of the group. The above assignments are tentative.

The frequency of these vibrations strongly depends on the type of substituent since there is a strong mechanical coupling between the deformation vibrations of the ester group and deformation vibrations of the substituents. The wavenumbers mentioned above, therefore, can only be used as a guide to frequency position of the ester grouping. The first of these vibrations is especially sensitive to mechanical coupling and inductive effects and may be found in the region between  $650 \text{ cm}^{-1}$  and  $500 \text{ cm}^{-1}$ . Also, the intensity has been found to vary strongly. The assignment follows the one suggested by Katon and Bentley<sup>192</sup> for similar vibrations of ketones.

More detailed information on the far infrared absorptions of esters is available from a recent publication of Lucier and Bentley.<sup>193</sup>

## 2. Oil-Free Alkyd Resins

Oil-free alkyd resins, or "glyptals," are polyesters of phthalic acid with tri or polyvalent alcohols like glycerol or pentaerythritol. The spectral pattern in the far infrared is governed by the absorptions of the

ester groups and the aromatic ring system. Different kinds of alcohols have only a slight influence on the far infrared spectrum. All types of phthalic acid esters possess a sharp band at  $650\text{ cm}^{-1}$  (Figure 39). This may be assigned to the degenerate bending vibration of the ester group since the highest in-plane bending vibration of the orthosubstituted benzene ring, according to Jacobsen<sup>110</sup>, absorbs at lower frequencies between  $495\text{ cm}^{-1}$  and  $555\text{ cm}^{-1}$ . However, this assignment is not very suitable since a bending vibration of the ester group should exhibit at least some sensitivity to the kind of the substituent. Also, characteristic for the ester group but less obvious are bands around  $415\text{ cm}^{-1}$  and  $350\text{ cm}^{-1}$ . The band near  $562\text{ cm}^{-1}$  can possibly be assigned to the in-plane bending vibration of the aromatic ring.

Spurr et al<sup>194</sup> studied the infrared spectrum of diallyl phthalate polymers. The far infrared spectrum of a diallyl phthalate pre-polymer (Figure 40) is rather similar to that of oil-free alkyd resins.

### 3. Oil-Modified Alkyd Resins

Oil-modified alkyds are widely used for lacquers and paints. The ones containing a high percentage of highly unsaturated vegetable oils are air-drying. Those containing smaller percentages of oil ("short-oil" alkyds), or mainly saturated fatty acids, have to be cured at higher temperatures.

Isolated and conjugated olefinic double bonds in trans-configuration absorb between  $980\text{ cm}^{-1}$  and  $950\text{ cm}^{-1}$ . Cis-olefinic groups prevailing in natural oils have a broad absorption around  $730\text{ cm}^{-1}$  which is merged with the methylene rocking vibration at about  $730\text{ cm}^{-1}$  of the long aliphatic chains. There is no infrared spectroscopic method for the direct determination of the cis-content in oils because this band is too diffuse and

inseparable from the methylene-rocking vibration. Unfortunately, there seems to be no useful absorption of cis-vinylene groups in the far infrared either.

Oil-modified alkyd resins in their far infrared spectra (Figures 41-44) differ from the oil-free alkyds by a rather significant band at about  $480\text{ cm}^{-1}$ . This band seems to belong to a vibration of the ester group in long-chain esters.

The far infrared absorptions of vegetable oils are generally weak. If the oils for practical purposes are modified with strongly absorbing resins like the epoxy resins, then the spectrum of this modified oil is very similar to that of the pure modifying resin. The spectrum of an epoxy-modified dehydrated castor oil (Figure 45) is very similar to that of a pure epoxy resin (Figure 93).

Oil-modified alkyd resins based on isophthalic acid differ only slightly in their far infrared spectrum (Figure 46) from the alkyd resins based on phthalic acid. There is normally a pair of bands or a broad band somewhere near  $630\text{ cm}^{-1}$  where o-phthalates have a single and sharp band. The maximum of the broad band of o-phthalates near  $350\text{ cm}^{-1}$  shifts to about  $340\text{ cm}^{-1}$  in the spectrum of isophthalates.

#### 4. Terephthalic Acid Polyesters.

a. Polyethylene terephthalate. Polyethylene terephthalate was first developed by the ICI on a technical scale and is now widely used as a very tough and resistant material for films (Mylar, Hostaphan) and fibers (Terylene). The monomer unit is:  $-O-CH_2-CH_2-O-C(=O)-\text{C}_6\text{H}_4-C(=O)-$ . The polymer can be crystallized to a rather high percentage of crystallinity. The

# Contrails

crystal structure was studied by X-ray diffraction by a number of authors.<sup>195-198</sup> According to Daubeny et al.<sup>195</sup> the unit cell contains one monomer unit, is triclinic, and has the following dimensions:  $a = 4.56 \text{ \AA}$ ,  $b = 5.94 \text{ \AA}$ ,  $c = 10.75 \text{ \AA}$ ,  $\alpha = 98 \frac{1}{2}^\circ$ ,  $\beta = 118^\circ$ ,  $\gamma = 112^\circ$ . This gives the density of the crystals as  $1.455 \text{ g cm}^{-3}$ . The entirely amorphous material has a density of  $1.335 \text{ g cm}^{-3}$ .

The molecules in the unit cell are nearly co-planar. The unit cell has a center of symmetry. A slight deviation from planarity results from the COO groups being about  $12^\circ$  out of the plane of the benzene rings. It is also thought that the  $\text{CH}_2\text{-CH}_2$  bond is rotated about  $20^\circ$  around the  $\text{O-CH}_2$  bond from the planar configuration.

The infrared spectrum of the polymer is very complex due to the large number of atoms in the monomer unit. Consequently definite assignments of the bands to certain vibrational modes have not been obtained despite the large number of investigators.<sup>199-210</sup> A comprehensive study of the infrared spectrum of oriented films of polyethylene terephthalate was published by Liang and Krimm<sup>206</sup> and by Krimm.<sup>3</sup> The far infrared bands and their assignment, given in the latter paper, are reproduced in Table 20, together with our results. Figure 47 shows a commercial film of polyethylene terephthalate.

A number of authors were especially interested in the effects of crystallinity on the infrared spectrum of polyethylene terephthalate.<sup>199,200,205,206,210</sup> The intensity of a relatively large number of bands is a function of the crystallinity of the specimen. Table 21 shows bands whose frequency and intensity depend on the crystallinity of a sample (according to Tadokoro et al.<sup>209</sup>). There is a pronounced increase in absorptions at  $1340 \text{ cm}^{-1}$  and  $972 \text{ cm}^{-1}$  upon crystallization of the polymer.<sup>199,200</sup> An "amorphous" band according to Miller and Willis<sup>200</sup> which is not sensitive to the orientation of the sample is the medium absorption near  $898 \text{ cm}^{-1}$ .

TABLE 20

Far Infrared Absorptions of Polyethylene Terephthalate

<u>Krimm<sup>3</sup></u>	<u>This Report</u>	<u>Dichroic Behavior</u>	<u>Assignment<sup>(a)</sup></u>
<u>Wavenumber, cm<sup>-1</sup></u>			
680	678	⊥	$\gamma_{4}(B_2) ?$
633	630		combination $\gamma'_{18B} + \delta(C-O-C)$
613	610 br	⊥	$\gamma_{6B}(B_1) ?$
575	-		combination $\gamma_{10B} + \gamma_{16B}$
525	520 br		$\gamma_{6A}(A_1)$
502	504		$\gamma_w(C=O)$
437	?		$\delta(CCO)$
430	431	⊥	$\gamma_{16B}(B_{1u})$
383	377		$\delta(COC)$
355	350	⊥	$\gamma_r(C=O)$
250	-	Not determined	$\gamma'_{18B}(B_{2u})$
145	-	Not determined	
approx. 95		Not determined	

br = broad

(a) For the form of the normal modes, see Liang and Krimm<sup>206,114</sup> and Pitzer and Scott.<sup>211</sup>



TABLE 21

Infrared Bands of Polyethylene Terephthalate Sensitive to  
Crystallization According to Tadokoro et al<sup>209</sup>

<u>Crystalline</u>	<u>Amorphous</u>	<u>Molten</u>	<u>Relative Intensity<sup>(a)</sup></u>	<u>Changes with Crystallization</u>
<u>Wavenumber, cm<sup>-1</sup></u>				
3430	3432	3435	w	increase in intensity
3100	3100	-	vw	disappears in molten state
3011	-	-	vw	appears in crystalline form
1473	-	-	m	appears in crystalline form
1455	1455	1455	m	decrease in intensity
1378	-	-	vvw	appears in crystalline form
1371	1370	1368	w	decrease in intensity
1344	1339	1337	s	increase in intensity
1119	1117	1115(sh)	s	increase in intensity
1102	1100	1093	s	decrease in intensity
1040	1040	1035(sh)	w	distinguished in quenched samples, but not in the melt
970	970	962	m	increase in intensity
845	840	-	mw	increase in intensity, disappears in molten state

(a) w = weak, m = medium, s = strong, v = very, sh = shoulder

# Conclusions

There is a rotational isomerism in the  $-O-CH_2-CH_2-O-$  portion of the chain. Bands at 1470, 1340, 975, and  $850\text{ cm}^{-1}$  can be attributed to the trans-conformation of the  $CH_2$  groups in the crystalline regions, while bands at 1445, 1370, 1045, and  $900\text{ cm}^{-1}$  are to be associated with the gauche conformation of the  $CH_2$  groups. The latter is presumably to be found in the amorphous regions. Interestingly, most of the bands being sensitive to crystallinity belong to vibrational modes of the ethylene glycol units in the polymer.

The assignments were made with the assumption that the  $C-C_6H_4-C$  part of the chain can be classified in terms of the  $V_h$  symmetry of para-disubstituted benzene derivatives. However, a number of absorptions forbidden in the infrared but Raman active (exclusion rule) actually can be observed in the infrared spectrum. This is due to the loss of the center of symmetry by the rotation of chain members out of the plane of the benzene rings. For the assignment of the normal modes of the  $-O-CH_2-CH_2-O-$  unit, a symmetry  $C_{2h}$  for the trans 1,2-substituted ethane was assumed. This structure is implied by the molecular structure of crystalline polyethylene terephthalate according to Daubeny et al.<sup>195</sup>

In a recent study Schmidt<sup>210</sup> found that the trans form of the ethylene glycol linkage is the extended form, and the gauche form is the relaxed form. The amorphous regions of polyethylene terephthalate have been found to contain both of these isomers.

b. Polyester Resins Based Upon Terephthalic Acid. The principal use of terephthalic acid polyesters other than those with ethylene glycol are for wire enamels. Usually a mixture of glycerol and ethylene glycol is used for the esterification of the acid. The resulting polyester contains a

considerable number of free hydroxyl groups which crosslink at higher temperatures. The resin is poorly soluble in the usual solvents but readily soluble in a technical mixture of phenols, cresols, and xylenols.

The infrared and gas-chromatographic analysis of lacquers of this type was described by Hummel.<sup>212</sup> The far infrared spectrum (Figure 48) is distinctly different from that of polyethylene terephthalate. This is mainly due to the high crystallinity of the latter. Surface coating resins based on terephthalic acid are amorphous.

## 5. Styrenated Alkyd Resins and Vegetable Oils

Oil-modified alkyd resins can be further modified with styrene. The reaction takes place at the double bonds of the unsaturated fatty acids of the oil-component and polystyrene chains of different length are formed. Surface coatings with this type of resins show higher resistance against aging and chemicals.

The far infrared spectrum of a styrenated alkyd resin (Figure 49) shows the strong band of polystyrene around  $540\text{ cm}^{-1}$  superimposed by the strong and broad band of alkyds near  $560\text{ cm}^{-1}$ .

Vinyl toluene can be used instead of styrene as a modifying agent, and unsaturated vegetable oils in place of alkyd resins. In the far infrared spectrum of a vinyl-toluene modified vegetable oil (Figure 50) a band near  $440\text{ cm}^{-1}$  is characteristic for the polymeric vinyl toluene component.

## 6. Unsaturated Polyester Resins

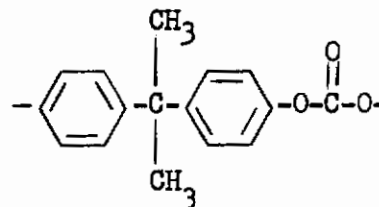
The conventional unsaturated polyester resins are usually based upon a polyester from maleic acid, phthalic acid, adipic acid and a glycol. However, there are many variations in the type of unsaturated and saturated acids, and also in the kind of diols, to meet certain industrial specifica-

tions. These resins are dissolved in styrene or in another suitable monomer like diallyl phthalate or triallyl cyanurate. The depolymerization is usually initiated by the addition of a radical catalyst.

For the identification of an uncured sample, the resin and the monomer are separated by evaporation or by suitable solvents. The far infrared spectra of styrene-free samples (Figures 51 and 52) show the characteristic band of phthalic acid esters at  $650\text{ cm}^{-1}$ , together with bands of the other components at  $670$ ,  $640$ , and  $563\text{ cm}^{-1}$ . However, this picture may change considerably from one type of unsaturated polyester to another.

## 7. Polycarbonates

The most interesting polyester of carbonic acid is based on bisphenol A, and has the following monomer unit:



It has found considerable use as a thermoplastic material for heat-resistant household items and films. A structure for the molecule in the crystalline regions of the polymer has been proposed by Prietzschk<sup>213</sup> on the basis of preliminary X-ray diffraction studies. However, Krimm stated in a recent publication<sup>214</sup> that this proposed structure is in significant disagreement with X-ray and infrared data.

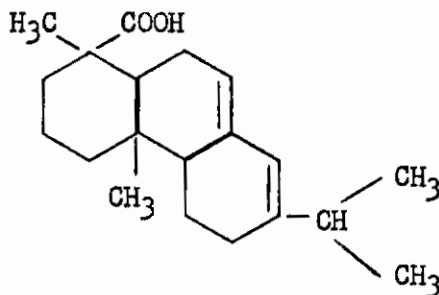
The far infrared spectrum of a film of polycarbonate on base of Bisphenol A (Figure 53) shows only one strong band at  $555\text{ cm}^{-1}$ , which is also present in the spectra of epoxy resins based on Bisphenol A. This band must be assigned to an out-of-plane bending vibration of the para-substituted benzene ring; its wavenumber is in very good agreement with the value

calculated by Shimanouchi et al.<sup>100</sup> (see Table 8). Bands at about 630, 485, and 350 or 390  $\text{cm}^{-1}$  probably belong to deformation vibrations of the  $-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$  group.

## 8. Rosin and Its Derivatives, Other Natural Resins

Natural resins can be divided into three large groups according to their chemical structure: acid resins, ester resins, and hydrocarbon resins. There is, however, no clean separation between these groups. Natural resins are usually complex and not yet fully analyzed mixtures containing acids, esters, and other compounds of mainly hydrocarbon nature.

Rosin from conifers consists mainly of abietic acid and isomeric abietic acids. The structure



is too complicated

for a complete infrared analysis. However, the di- $\alpha$ -branched carbonyl group behaves exactly like the other carboxylic acids of this type studied by Bentley et al.<sup>215</sup> These authors found for di- $\alpha$ -branched aliphatic acids one strong band between about 610  $\text{cm}^{-1}$  and 665  $\text{cm}^{-1}$ . There is a strong band at 657  $\text{cm}^{-1}$  in the far infrared spectrum of rosin (Figure 54). Another medium to strong band characteristic for both mono- and di- $\alpha$ -branched aliphatic acids appears between 520  $\text{cm}^{-1}$  and 555  $\text{cm}^{-1}$ . Rosin shows this band at about 538  $\text{cm}^{-1}$ . Both bands are bending vibrations of the associated carboxylic groups.

Rosin glyceryl ester (Figure 55) has a number of bands in common with rosin itself: 704, 606, 562, and 483  $\text{cm}^{-1}$ ; it is not unlikely that some of these bands are characteristic for the molecular skeleton of abietic acid.

Maleinate resins are obtained by a Diels-Alder addition of maleic anhydride to rosin. They are usually esterified with polyvalent alcohols. The far infrared spectrum of a maleinate resin (Figure 56) also shows the bands at 604, 560, and around 475  $\text{cm}^{-1}$  possibly characteristic for derivatives of abietic acid.

Guaiac is a dark-green to brown-black resin obtained from the trunk of *Guaiacum officinale*. It contains about 70% guaiaconic acid and some other acid and neutral compounds. The bands at about 620, 555, and 440  $\text{cm}^{-1}$  in its far infrared spectrum (Figure 57) are characteristic for the acid constituents.

## 9. Polyvinyl Acetate.

Vinyl acetate is readily polymerizable with radical catalysts. The amorphous polymers can have molecular weights up to about  $5 \times 10^5$ , and are highly branched. They have found widespread use as binders in surface coatings and cements, for fuel-resistant pipes, and so on.

The infrared spectrum of polyvinyl acetate was studied by Melville et al.<sup>216</sup>, the Raman spectrum by Simon et al.<sup>217</sup> The strongest band in its far infrared spectrum (Figure 59) is at 605  $\text{cm}^{-1}$ ; a corresponding Raman band was found at 606  $\text{cm}^{-1}$  (Simon et al.<sup>217</sup>). This absorption has to be assigned to a bending vibration of the acetate group. Thompson and Torkington<sup>218</sup> described two bands in the far infrared as being characteristic for acetates; one near 612  $\text{cm}^{-1}$ , the other near 640  $\text{cm}^{-1}$ . The band at 630  $\text{cm}^{-1}$  in the spectrum of polyvinyl acetate may be this second acetate band. A fairly strong Raman line is found at 632  $\text{cm}^{-1}$ . Most of the other far infrared bands are paralleled by corresponding Raman lines except the one at about 511  $\text{cm}^{-1}$ . On the other hand, a very weak Raman line at 462  $\text{cm}^{-1}$  has no

corresponding line in the infrared. Both are weak and may be due to bending vibrations of the polyvinyl chain.

## E. Polymers of Acrylic and Methacrylic Acids and Esters (Chart V)

### 1. Polyacrylic acid and Polymethacrylic acid; Salts of These Acids.

The far infrared spectrum of polyacrylic acid (Figure 60) shows three fairly strong bands near 630, 515, and 350  $\text{cm}^{-1}$ . The first two bands are found in the ranges which were given by Bentley et al.<sup>215</sup> for mono- $\alpha$ -branched carboxylic acids. The band at 350  $\text{cm}^{-1}$  probably belongs to an out-of-plane deformation vibration of the associated carboxyl groups. Part of the Raman spectrum of polyacrylic acid was published by Simon et al.<sup>217</sup>

The far infrared spectrum of polymethacrylic acid (Figure 65) is markedly different from that of polyacrylic acid. The first two far infrared bands of  $\alpha$ -branched carboxylic acids are found here at 612  $\text{cm}^{-1}$  and 535  $\text{cm}^{-1}$ . A new band appears near 270  $\text{cm}^{-1}$  and may be due to a methyl torsion vibration.

The far infrared spectrum of the sodium salt of polyacrylic acid (Figure 61) is not very pronounced. Three bands near 650, 570 and 350  $\text{cm}^{-1}$  are observed above a high background. The 650  $\text{cm}^{-1}$  band is very likely due to the OCO inplane bend. The bands at lower wavenumbers may be due to wagging, rocking or twisting vibrations of the carboxylate ion. Wilmshurst<sup>219</sup>, in his comprehensive study of COOX compounds, has also briefly discussed the far infrared absorption of carboxylic salts.

### 2. Polyacrylic esters.

Esters of acrylic acids with lower aliphatic alcohols polymerize

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readily with radical catalysts to form polymers with lower softening points than the corresponding polymethacrylic esters. With increasing molecular weight of the alcoholic component the polymers gradually become soft resins.

The monomer unit  $\begin{array}{c} -\text{CH}-\text{CH}_2- \\ | \\ \text{COOR} \end{array}$  in polyacrylic esters contains an asymmetric

carbon atom. Consequently, stereospecific polymerization of acrylic esters leads to the formation of isotactic or syndiotactic polymers. Stereospecific catalysts for the polymerization of monomers containing electronegative groups are organometallic compounds like lithium-butyl, lithium-phenyl, phenyl-magnesium bromide, and others. Interestingly, Garrett et al<sup>220</sup> show for the acrylic esters that low temperatures  $\langle -70^\circ\text{C}$  favor the syndiotactic addition of monomer units to a growing chain so that radical initiation by ultraviolet or  $\gamma$ -radiation yields crystallizable polymers.

The following authors studied the infrared spectra of stereoregular polyacrylic esters: Miller and Rauhut<sup>221,222</sup>, crystalline p-tert-butyl acrylate; Garrett et al<sup>220</sup>, crystalline polyalkyl acrylates with different alkyl substituents; Kawasaki et al<sup>223</sup>, stereoregular polymers of n-, sec-, and tertbutyl acrylate; Kawasaki et al<sup>224</sup>, stereoregular polyethyl- and polypropyl thiolacrylates; Nakayama et al<sup>225</sup>, stereoregular polyalkyl thiolacrylates.

Part of the Raman spectrum of polyethyl acrylate was published by Simon et al.<sup>217</sup> The infrared spectra of copolymers of styrene with acrylic acid derivatives were studied by Theyssie and Smets.<sup>226</sup> Schurz et al<sup>227</sup> studied the infrared spectra of all kinds of polyacrylic acid derivatives.

The far infrared spectra of polyacrylic esters with unbranched alkyl substituents (Figures 62-64) are somewhat surprising in that they do not show an absorption of significant intensity between about  $550\text{ cm}^{-1}$  and



650  $\text{cm}^{-1}$  (see Lucier and Bentley<sup>193</sup>). This may be due to the  $\alpha$ -branching of the ester group. The strongest band appears between 370  $\text{cm}^{-1}$  and 330  $\text{cm}^{-1}$ ; with increasing size of the side chain, its maximum shifts to lower wavenumbers. A second broad and intense band arises at the short-wavelength flank of the main absorption. It also seems to shift to lower wavenumbers with increasing size of the side chain.

### 3. Polymethacrylic esters

Methacrylic acid esters polymerize readily with radical catalysts to form non-crystallizable and probably mainly atactic polymers. Polymethacrylates are more rigid than the corresponding polyacrylates, and have found widespread use in industry.

A comprehensive study on the infrared spectra of methacrylic esters and their polymers was done by Salomon et al.<sup>228</sup> The far infrared was covered between 700  $\text{cm}^{-1}$  and 400  $\text{cm}^{-1}$ . Our own results agree well with those of the authors mentioned. An infrared spectroscopic method for the determination of double bonds in polymethyl methacrylate was developed by Loshak and Fox.<sup>229</sup> The infrared spectra of styrene-methyl methacrylate copolymers were studied by Axelrod.<sup>230</sup> Stroupe and Hughes<sup>231</sup> published a study on the structure of polymethyl methacrylate.

By the use of stereospecific catalysts previously described for polyacrylates in this report, stereoregular and crystallizable polymers can be obtained. Fox et al.<sup>232</sup> described three types of polymethyl methacrylate with different X-ray patterns and different other properties both in the crystalline and amorphous states (see Table 22).

In another publication, Fox et al.<sup>233</sup> stated that for steric reasons isotactic addition of monomer units to growing chains should be favored at

TABLE 22  
Properties of Different Polymethyl Methacrylates<sup>232</sup>

<u>Type</u>	<u>Glass Temp., °C</u>	<u>Melting Point, °C</u>	<u>Density, 30°C (Amorphous) g ml<sup>-3</sup></u>	<u>Polymerization Conditions</u>	<u>Presumed Chain Configuration</u>
I	115	200	1.19	Free radical at low temp.; anionic in highly solvating media	Isotactic, crystallizable
II	45	160	1.22	Organo-lithium cpds. (anionic) in hydrocarbons	Syndiotactic, crystallizable
III	60-95	170	1.20-1.22	Anionic at low temp. in media of moderate solvating power for cations	Isotactic-syndiotactic block-copolymer
Conventional	104	-	1.188	Radical catalysts at room temp.	Essentially random

# Contrails

lower temperatures, whereas higher polymerization temperatures should favor syndiotactic growth.

The infrared spectra of stereoregular polymethyl methacrylates were studied by a number of authors.<sup>233-239</sup> Fox et al<sup>233</sup> found large spectral differences near  $1065\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$  in the spectra of differently polymerized samples, both in the crystalline and in the amorphous states. Miller et al<sup>234</sup> found characteristic bands near  $955\text{ cm}^{-1}$  and  $755\text{ cm}^{-1}$  in the spectrum of a crystalline polymer of presumable isotactic structure; bands present in the spectrum of a conventional polymer near  $1063$ ,  $965$ ,  $913$ ,  $825$ , and  $747\text{ cm}^{-1}$  were missing. Baumann et al<sup>235</sup>, on the other hand, found no bands characteristic for an isotactic structure in the rocksalt range. They noted, however, that bands near  $1475$ ,  $1060$ ,  $965$ ,  $909$ ,  $824$ , and  $806\text{ cm}^{-1}$  present in the spectra of both syndiotactic and conventional polymethyl methacrylates are missing in the spectrum of an isotactic polymer. Most obvious is the disappearance of a band near  $1060$  in the spectrum of isotactic samples. From their results, Baumann et al<sup>235</sup> concluded that conventional polymethyl methacrylate has a structure with exceeding syndiotactic arrangement. Fox et al<sup>233</sup>, Baumann et al<sup>235</sup>, and Kawasaki et al<sup>236</sup> found that a number of bands, especially those near  $1060\text{ cm}^{-1}$ , can be found almost unchanged also in the spectra of dissolved or amorphous syndiotactic. (The "F-polymer" of Kawasaki et al is probably identical to the "isotactic" samples of other authors.) Korotkov et al<sup>238</sup> describe bands near  $962\text{ cm}^{-1}$  and  $854\text{ cm}^{-1}$  as characteristic for isotactic polymethyl methacrylate which are missing from the spectrum of a conventional polymer.

The results of the different authors on the infrared spectrum and structure of different samples of polymethyl methacrylate are partially contradictory and do not yield a clear picture. However, it can be accepted as

established that there exist different crystallizable polymers of methyl methacrylate which are non-polymorphous to each other and possess different stereoregular structures. As to the conventional polymethyl methacrylate, it is rather likely that it contains a large number of syndiotactic arrangements.

The far infrared spectrum between  $15 \mu$  and  $24 \mu$  of different samples of polymethyl methacrylate was studied by Hummel and Busse<sup>128</sup> (see Figures 66 and 67). These authors found a band near  $557 \text{ cm}^{-1}$  which is much stronger in isotactic than in syndiotactic samples. The maximum of the band in syndiotactic samples is near  $552 \text{ cm}^{-1}$ . A doublet with maxima at about  $506 \text{ cm}^{-1}$  and  $482 \text{ cm}^{-1}$  is also sensitive to tacticity. The component at  $506 \text{ cm}^{-1}$  increases with the increasing amount of sample consisting of syndiotactic structures.

Figure 68 shows a sample which was prepared by polymerization at  $100^\circ\text{C}$  with dibenzoyl peroxide. The shape of the doublet with maxima near  $480 \text{ cm}^{-1}$  and  $506 \text{ cm}^{-1}$  lies between the extremes represented by isotactic (Figure 66) and syndiotactic samples (Figure 67).

The spectra of higher polymethylmethacrylates (Figures 69-71) show that substituents definitely influence the frequency position of the vibrations of the ester group. Thus, polymethyl methacrylates can easily be identified by their far infrared spectra.

## F. Cellulose Derivatives (Chart VI)

### 1. Regenerated Cellulose and Cellulose Ethers.

The far infrared spectra of cellulose (Figure 72) and its alkyl ethers (Figures 73 and 74) show a broad absorption band ranging from about  $700 \text{ cm}^{-1}$  to  $300 \text{ cm}^{-1}$ . We have to assume that the bending vibrations of the

glucose units and the substituents are strongly coupled. In other words, the high absorption background is proof for strong intra and probably intermolecular interactions. From an analytical standpoint, the far infrared spectra of cellulose ethers are of little value.

## 2. Cellulose Esters.

The far infrared spectra of cellulose esters (Figures 75 to 79) are more significant than those of the ethers. Cellulose nitrate (Figure 79), binder from "Duco Cement") is one exception, since organic nitrates do not have strong far infrared absorptions. The strongest band in the far infrared spectra of the carboxylic acid esters is around  $600\text{ cm}^{-1}$ . It probably belongs to a bending vibration of the acyl groups attached to the secondary CH-O groups in the glucose units.

## G. Polyethers and Ether Resins (Chart VII)

### 1. Linear Aliphatic Polyethers

Linear aliphatic polyethers with the general structure  $[(\text{CH}_2)_m\text{O}]_n$  can be prepared by polymerization of the cyclic oxides of the general formula  $(\text{CH}_2)_n\text{O}$ . The polymerization usually has an anionic mechanism and can be initiated, for example, by bases or Lewis bases.

Linear aliphatic polyethers usually have a helical structure.

Miyazawa<sup>240</sup> described a general method of normal coordinate treatment by internal coordinates for the vibrational spectra of chain molecules of the general structures  $(\text{CH}_2)_n$ ,  $(\text{CH}_2\text{O})_n$ , and  $(\text{CH}_2\text{OCH}_2)_n$ . Tadokoro<sup>11,12</sup> derived a method for the numerical calculation of the normal vibrations of helical molecules and used it for the evaluation of the infrared spectrum of polyoxymethylene.

# Contrails

a. Polyoxymethylene. The first member of the series of cyclic aliphatic oxides is formaldehyde ( $n = 1$ ). It polymerizes readily on standing and forms a crystalline and brittle polymer called "paraformaldehyde," which is a mixture of polymers containing between 8 and 100 monomer units. It took twelve years and fifty million dollars to develop a polyoxymethylene which has a very high molecular weight and is known as "Delrin" (Figure 80) and manufactured by Dupont. Recently, Celanese announced a similar polymer.<sup>241</sup>

The technical polyoxymethylene is highly crystalline, has blocked end-groups to prevent zip-depolymerization, and is soluble only in a few solvents like hot dimethyl sulfoxide or dimethyl formamide. It has a helical structure with nine monomer units and five turns in the identity period of  $17.3 \text{ \AA}$ . Its infrared spectrum, and the spectrum of lower polyformaldehydes, was studied by a number of authors.<sup>11,12,242-246</sup>

The far infrared spectrum of polyoxymethylene was studied in detail by Tadokoro et al.<sup>244,245</sup> The results of these authors, together with our own, are shown in Table 23.

Complete assignments of the infrared bands of polyoxymethylene and polyoxymethylene- $d_2$  are given in the recent paper of Tadokoro et al.<sup>246</sup>

b. Polyoxyethylene. Ethylene oxide,  $\text{CH}_2\text{-CH}_2$ , can be polymerized to form liquid or wax-like polymers. In the absence of water and other chain-terminating reagents, fibrous high-polymers with molecular weights around  $10^6$  can be obtained. In contrast to polyoxymethylene, these polymers are readily soluble in water up to the highest molecular weights obtained. Apparently the intermolecular interactions between the polyoxyethylene chains

TABLE 23

Far Infrared Absorptions of Helical,  
Crystalline Polyoxymethylene ("Delrin")

<u>Literature Data<sup>244, 245</sup></u>	<u>This Report</u>	<u>Dichroic Behavior</u>	<u>Assignment</u>
<u>Wavenumber, cm<sup>-1</sup></u>			
630-633	629	⊥	$\delta(\text{O-C-O}) (E_1) (90\%),$ mixed with $\nu_2(\text{C-O-C})$
455-458	450	⊥	$\delta(\text{C-O-C}) (E_1) (76\%),$ mixed with $\nu_7(\text{CH}_2)$
235	Not determined		Torsional Vibration of the C-O-C chain, $A_2$
22 (calculated)	Not determined	Not determined	Torsional vibration of the C-O-C chain, $A_1$

# Contrails

are lower, and allow the water molecules to separate the chains by forming hydrogen bridges.

Crystalline polyoxyethylene also has helical chains with a fiber period of 19.25 Å. Davison<sup>247</sup>, from his infrared data, assumed a threefold helix and a gauche-conformation of the monomer units. Miyake<sup>248</sup> later altered Davison's assignments and assumed monomer units in both the trans and gauche-conformations. Miyazawa et al<sup>249</sup> did not agree with the earlier assignments and conclusions and made another careful examination of the infrared spectrum between 3500 cm<sup>-1</sup> and 50 cm<sup>-1</sup> of highly oriented crystalline films. Measurements with polarized infrared were done between 3500cm<sup>-1</sup> and 400 cm<sup>-1</sup>. According to these authors, the most likely model with trans-gauche-trans conformation contains seven monomer units and two helical turns per fiber period of 19.25 Å.

Low molecular weight polyoxyethylene glycols are liquids. The infrared spectra were studied by Davison<sup>247</sup>, and Kuroda and Kubo.<sup>250,251</sup> The far infrared spectrum of a liquid polyoxyethylene glycol (Figure 81) shows only one fairly strong absorption band due to a C-O-C bending vibration with a maximum ranging between 560 cm<sup>-1</sup> and 520 cm<sup>-1</sup>. A second broad band near 260 cm<sup>-1</sup> is probably due to a torsional vibration of the chain.

The far infrared spectrum of a highly crystalline polyoxyethylene with a molecular weight about 8.10<sup>5</sup> (Figure 82) differs strongly from that of a liquid polyoxyethylene glycol. The C-O-C bending vibration has split into two components at 527 cm<sup>-1</sup> and 507 cm<sup>-1</sup>, and a number of new, weak bands has appeared at the red end of the spectrum. The results of Miyazawa et al<sup>249</sup> together with ours are shown in Table 24.



TABLE 24

Far Infrared Bands of Polyoxyethylene

<u>Miyazawa et al</u> <sup>249</sup>	<u>This Report</u>	<u>Dielectric Behavior</u>	<u>Potential Energy Distribution (%)</u>
<u>Wavenumber cm<sup>-1</sup></u>			
	640	Not determined	
	577)	Not determined	
	560)	Not determined	
529	527)		$\delta(\text{CCO}) (A_2) (100)$
508	507)		
(485)*	455 (sh)	Not determined	
(372)*	380	Not determined	
	355	Not determined	
	324	Not determined	
216		⊥	$\delta(\text{CCO}) (35), \gamma_t(\text{CC}) (35),$ $\delta(\text{COC}) (25); E(\theta)$
165		⊥	$\gamma_t(\text{CO}) (35), \gamma_t(\text{CC}) (30),$ $\delta(\text{CCO}) (25); E(\theta)$
107			$\gamma_t(\text{CO}) (85)$

\*Calculated but not observed by Miyazawa et al.<sup>249</sup>

c. Polyoxypropylene. Propylene oxide,  $\text{CH}_2-\overset{*}{\underset{\text{O}}{\text{C}}}-\text{CH}_3$ , has an

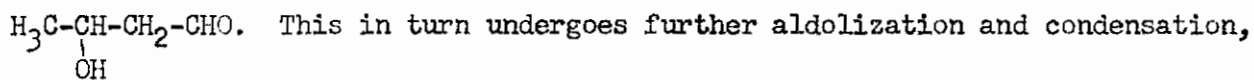
asymmetric carbon atom in its molecule, and consequently can occur in a d- and in an l-form. Price et al.<sup>252</sup> described the formation of a crystallizable and optical active polyoxypropylene by the polymerization of l-propylene oxide. They explained the optical activity with an all-l structure of the polymer. Other polymerization conditions yielded a crystallizable but optical inactive polymer apparently consisting of a racemic mixture of all-d and all-l forms. The infrared spectrum of crystalline polyoxypropylene was described by Price and Osgan<sup>253</sup> and Kawasaki et al.<sup>254</sup>

With normal ionic catalysts and with the racemic mixture of propylene oxide liquid or paste-like polymers with relatively low molecular weight are formed. Only the lower members of the homologous series show a slight solubility in water.

The far infrared spectrum of a liquid polyoxypropylene (Figure 83) is rather indistinct. A very broad band between  $600 \text{ cm}^{-1}$  and  $400 \text{ cm}^{-1}$  is due to bending vibrations of the C-O-C groups, and out-of-plane deformation vibrations of hydroxyl end-groups.

## 2. Other, Ill-Defined Polyethers

Another group of resinous aliphatic ethers are the self-condensation products of aldehydes and ketones. Acetaldehyde aldolizes to yield

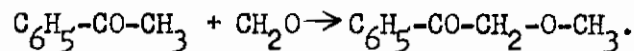


This in turn undergoes further aldolization and condensation, a process which finally yields a resin-like material containing alcoholic and ether groups, and also some unreacted aldehyde groups.

An infrared study on polyacetaldehyde was published by Delzenne and Smets<sup>255</sup>. The far infrared spectrum of an obsolete industrial acetaldehyde

resin (Figure 84) is very poor. The very broad absorption between  $700\text{ cm}^{-1}$  and  $440\text{ cm}^{-1}$  is caused mainly by C-O-C and C-OH deformation vibrations. The assignment of the weak but sharp band at about  $365\text{ cm}^{-1}$  is unknown.

A technical condensation product of acetophenone with formaldehyde is used as unsaponifiable resin in surface coatings. According to its infrared spectrum, it did not contain hydroxyl groups. On the other hand, many of the  $\text{C}_6\text{H}_5\text{-C}\begin{array}{c} \parallel \\ \text{O} \end{array}$  residues apparently remained unchanged. This leads to the assumption that the condensation process mainly includes the activated methyl groups:



This keto-ether may further react with its activated methylene group. The far infrared spectrum (Figure 85) contains a number of weak and medium absorption bands, some of which may be assigned to ring vibrations. There is no strong bending vibration of ether groups evident.

### 3. Polyvinyl Ethers.

Vinyl ethers polymerize in the presence of Lewis acids to form amorphous polymers of a soft-resin, or rubber-like nature (see Schildknecht et al.<sup>256</sup> Since there is one asymmetric carbon atom in the monomer unit,  $\text{-}\underset{\text{OR}}{\text{CH}}\text{-CH}_2\text{-}$ , stereoregular polymers with isotactic or syndiotactic structure must be possible. Schildknecht et al.<sup>257</sup> polymerized vinylisobutylether, in analogy to a former German patent of Mueller-Gunradi and Pieroh, with  $\text{BF}_3$ -dialkylether complexes ("modified Friedel-Crafts catalyst") and obtained rather rigid polymers. These could be fractionated and yielded crystallizable fractions. Later, Natta and his coworkers<sup>258,259</sup> were able to obtain a number of isotactic, crystallizable polyvinylethers using

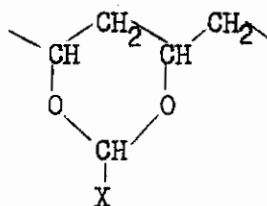
modified Friedel-Crafts catalysts.

The infrared spectra of some polyvinyl ethers were published by Schildknecht.<sup>260</sup> The far infrared spectrum of an amorphous polyvinyl methyl ether (Figure 86) shows two strong bands at about  $550\text{ cm}^{-1}$  and  $410\text{ cm}^{-1}$ , rising above a rather high absorption background. These are probably bending vibrations involving the ether group.

The far infrared spectrum of an amorphous polyvinyl isobutyl ether (Figure 87) is more complicated. A number of bands are fused together in a broad absorption covering the range between  $600\text{ cm}^{-1}$  and  $350\text{ cm}^{-1}$ . Apparently the bending vibrations of the molecular skeleton couple strongly. The substitution of the methyl by an isobutyl group has put all the skeleton vibrations out of tune. This is consistent with the observation of Katon<sup>261</sup> that the far infrared absorptions of ethers cannot be considered as characteristic group frequencies.

#### 4. Polyvinyl Acetals.

Polyvinyl acetals can be obtained by the reaction of polyvinyl alcohol with aldehydes. Up to about 60% of the alcoholic groups thus are included in cyclic 1,3-dioxane structures:



hydrogen in the case of polyvinyl formal. The far infrared spectrum (Figure 88) of this polymer contains a sequence of medium to strong bands which may be assigned to in-plane and out-of-plane C-O-C bending vibrations of the dioxane ring systems. The spectrum of the butyral ( $X = C_4H_9$ ) (Figure 89) is less significant. The different bands are fused together in

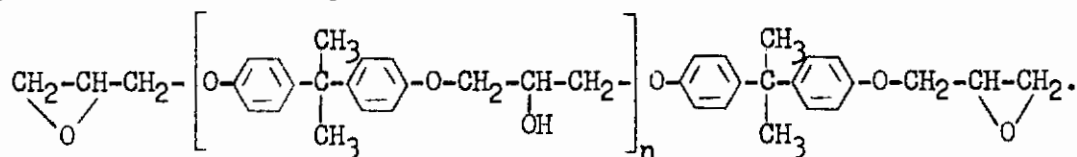
one very broad and intense band which covers the range between about  $700\text{ cm}^{-1}$  and  $350\text{ cm}^{-1}$ . This is one more example of the strong coupling of vibrations in the far infrared.

## 5. Epoxides.

Olefinic double bonds of the type  $-\text{CH}=\text{CH}-$  can readily be oxidized to form epoxy groups,  $-\text{CH}-\text{CH}-$ . The infrared absorption bands characteristic of the oxirane ring were studied by Patterson.<sup>262</sup> Isaac<sup>263</sup> investigated the far infrared spectra of epoxy compounds and reported a band at about  $370\text{ cm}^{-1}$  as being characteristic for the oxirane ring.

Figure 90 shows a aliphatic epoxy resin which contains alcoholic and ether groups in addition to the epoxy groups. The former gives rise to a very broad absorption band over the far infrared range. A superimposed band at about  $365\text{ cm}^{-1}$  possibly arises from the epoxy groups in the resin. In the spectrum of a highly epoxidized soy-bean oil (Figure 91), the strongest band at about  $460\text{ cm}^{-1}$  may be due to the epoxy groups.

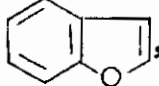
Widely used in surface coating resins and in castings are aromatic epoxy resins based on Bisphenol-A. The structure is:



Since the epoxy groups are only at the ends of the molecule, their relative concentration decreases with increasing molecular weight of the resin. The far infrared spectra of these compounds are very characteristic (Figures 91 and 92). Both an in-plane ring bending vibration and a C-O-C bending vibration contribute to the very strong absorption at about  $575$  to  $555\text{ cm}^{-1}$ .

The medium band at  $375\text{ cm}^{-1}$  in the spectrum of a low-molecular liquid of this type (Figure 91) belongs to the epoxy groups and can be used for quantitative measurements.

## 6. Coumaron Resins.

The olefinic double bond in coumarone, , is reactive. Polymerization is performed with acids like sulfuric acid, and leads to the formation of resinous polymers. Industrial coumarone resins contain up to 90% indene units.

The infrared spectra of industrial coumarone-indene resins were studied by Eckardt and Heinze.<sup>264</sup> The far infrared spectrum of a rather complex mixture of this type (Figure 94) has its strongest band near  $425\text{ cm}^{-1}$ . Polyindene also has its strongest far infrared band at this frequency.

## H. Phenolic Resins

The hydroxyl group on the phenyl ring activates the hydrogen atoms in the ortho and para position to the OH group. Those react with formaldehyde under acid or alkaline conditions to form "novolacs" or "resoles." The former contain roughly equimolecular amounts of phenol and aldehyde, and the links between the aromatic rings are methylene bridges. Resoles are formed with an excess of aldehyde and mainly under alkaline conditions. They are highly reactive and contain hydroxymethylene groups, methylene-ether bridges, and some methylene bridges. The hydroxyl group remains practically unchanged.

Ring-alkylsubstituted phenolic resins are widely used in surface coatings. The alkyl groups contain at least three carbon atoms. Tert butyl and tert-octyl are the principally used alkyls.

The infrared spectra of phenolic resins of all kinds were studied by a number of authors.<sup>265-272</sup> Soda<sup>271</sup> studied the structure of p-tert-butyl phenolic resins and  $\alpha$ -naphthol resins by their infrared spectra. His results in the far infrared are shown in Table 25. Since the solid resin is amorphous, it is not surprising that there is almost no difference in the spectra of the solid and the dissolved material. Conley and Bieron<sup>272</sup> studied the oxidation of phenol-formaldehyde polycondensates using infrared spectroscopy.

The far infrared spectra of different phenolic resins (Figures 95 to 100) were rather unpronounced and not of much use in the qualitative analysis. A high absorption background ranges from  $700\text{ cm}^{-1}$  to about  $300\text{ cm}^{-1}$ . As in the case of amorphous polyethers the bending vibrations of the different polar groups couple strongly, and only a few distinct bands rise above this absorption background.

To obtain more information in these cases, it is helpful to compensate the background with a grid or with another device thus making the bands more prominent. The spectrum of a cresole novolac (Figure 95) was obtained by this method.

## I. Nitrogen Containing Resins and Polymers (Chart VIII)

### 1. Polyamides

Polyamides are widely used as thermoplastics. They contain sequences of secondary amide groups and aliphatic groups. There are two main species of polyamides. The one has the general formula  $-R-CO-NH-R-CO-NH-$ , and is produced by the polymerization of cyclic amides (lactams). The other one has the general formula  $-R-CO-NH-R'-NH-CO-$ , and is formed by polycondensation of bifunctional acids and amines.

TABLE 25

Far Infrared Absorptions of a p-tert-Butylphenol Resin,  
According to Soda<sup>271</sup>

<u>Solid</u>	<u>Solution</u>	<u>Assignment</u>
<u>Wavenumber, cm<sup>-1</sup></u>		
685	685	Substituent-characteristic band
654	653	Substituent-characteristic band
600	600	
550	548	$\delta$ (OH) out-of-plane
521	522	$\delta$ (OH) out-of-plane
474	475	



# Contrails

If the aliphatic chains are simple methylene chains, the number of carbon atoms is denoted by a number added to the group-name "polyamide." Consequently, "polyamide 6" is a polyamide of the type I with a sequence of five methylene groups in the chain, whereas "polyamide 6,6" is a polyamide of the type II formed from adipic acid and hexamethylene diamine.

Polyamides with a regular structure have a great amount of crystallinity. This is mainly due to the hydrogen bridges connecting the polymer chains. By drawing out a fiber or film, more of the hydrogen bridges "snap in." This process is accompanied by changes in the infrared spectrum.

Copolyamides having different monomer units in a chain show a considerably lower degree of crystallization and also a lower melting range. On the other hand, they are more readily soluble in the conventional solvents and can be used as components in surface coatings.

The infrared spectra of polyamides were studied by a large number of authors.<sup>273-293</sup> The planar and strongly polar secondary amide group with its infrared active vibrations governs the spectrum of polyamides. The characteristic bands of the secondary amide group were numbered from I to VI. Actually, all of them are sensitive to the physical state of the sample. This is due to (1) the strong hydrogen bridges within and between the chains in solid or molten samples which may be partially broken in solutions, and (2) the strong mechanical coupling between different vibrational modes, for instance, between  $\nu(\text{C-N})$  and  $\delta(\text{NH})$ .

Table 26 shows the different characteristic bands of the secondary amide group in crystalline polyamides, together with their assignments. The values were partially taken from the literature, partially from our own spectra. A seventh amide band was added which probably has to be assigned to a torsional

TABLE 26

Characteristic Infrared Bands of Secondary Amides

<u>No.</u>	<u>Approximate Wavenumber, cm<sup>-1</sup></u>	<u>Assignment</u>	<u>Remarks</u>
I	1640	$\gamma$ (C = O)	
II	1545	$\gamma$ (C-N) + $\delta$ (NH)	Strong coupling
III	1280		
V	690	$\gamma$ (NH assoc.)	
IV	580	$\delta_{as}(O=C-N)^*$	Strong coupling between IV, VI, and VII
VI	520-550 (variable)	$\delta_s(O=C-N)^*$	
VII	290-400	$\gamma_t(O=C-N)^*$	

\*Assignment tentative.

# Contrails

vibration of the O=C-N group. Actually, the frequency range for this band is rather broad for one deserving the designation "characteristic frequency." However, it is a fairly strong band which can usually be identified without difficulty. In polyamides with the structure -R-CO-NH-R-CO-NH-, the amide-VII band is often found near  $300\text{ cm}^{-1}$ , whereas in polyamides with the structure -R-CO-NH-R'-NH-CO-, it is often found near  $350\text{ cm}^{-1}$  accompanied by a weaker band 30-50 wavenumbers higher. This observation, however, has to be confirmed by more experimental material.

The far infrared spectra of polyamides (Figures 101-108), generally speaking, are very characteristic and useful for qualitative and structural analysis.

Figure 102 (polyamide-6, polycaprolactam) was obtained from seven layers of a thin film which was previously oriented in two dimensions. Apparently, the degree of crystallinity is lower than in the sample obtained from formic acid solution (Figure 101). This is indicated by the higher background and the less prominent bands. Also, the intensity of the doublet at about  $725\text{ cm}^{-1}$  and  $690\text{ cm}^{-1}$  has reversed.

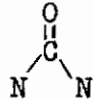
Copolyamides also show a lower degree of crystallinity. Hence, in the spectrum of a terpolyamide (formed from equal parts of hexamethylene diammonium adipate, caprolactam, and the adipate of p,p'-diamino-dicyclohexylmethane) the absorption background is high, and the absorption bands are broad (Figure 108).

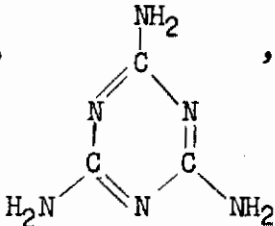
Polyamides of a special kind are the liquid or resin-like "Versamids." They are formed by condensation of di- and trimer unsaturated fatty acids with aliphatic polyamines. They contain free amine groups and are used as curing agents for epoxies. In the spectrum of one of these resins (Figure 109) the bands at about  $590$ ,  $520$ , and  $430\text{ cm}^{-1}$  originate from vibrations of the amide group.

## 2. Amino and Amido Formaldehyde Resins

Formaldehyde reacts with active hydrogen atoms of amino or amido groups to form methylol compounds which in turn are also highly reactive. For surface coating resins, these methylol compounds are partly etherified with butanol or other aliphatic alcohols; the rest serve for the crosslinking during the curing of the film.

The infrared spectra of urea-formaldehyde resins were studied by Becher.<sup>294</sup> He found that the primary methylol ureas in acid solution,  $\text{pH} < 3$ , react in the way of a condensation reaction and mainly form methylene ureas,  $[\text{H}(\text{NH}-\text{CO}-\text{NH}-\text{CH}_2)_n\text{NH}-\text{CO}-\text{NH}_2]$  plus some methylol methylene ureas,  $[\text{HOCH}_2(\text{NH}-\text{CO}-\text{NH}-\text{CH}_2)_n\text{CH}_2\text{OH}]$ . Excessive formaldehyde favors the formation of methylol groups. Acid-cured urea-formaldehyde resins contain only methylene bridges.

The far infrared spectrum of a butylated urea-formaldehyde resin (Figure 110) shows only one strong and broad band with its maximum around  $655 \text{ cm}^{-1}$ . A weak shoulder appears around  $540 \text{ cm}^{-1}$ . Both absorptions are very likely caused by bending vibrations of the  group, and of bending vibrations of the ether groups.

Melamine, , has six active hydrogen atoms which readily

react with formaldehyde to form methylol groups. These in turn can be etherified, or react with amino hydrogen or other methylol groups. Melamine resins have obtained considerable application for mouldings and in surface coating lacquers.

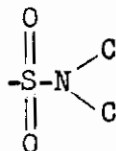
# Contrails

The infrared spectra of triazine derivatives were studied by a few authors.<sup>295-297</sup> The infrared spectra of melamine and melamine-d<sub>6</sub> were investigated by Jones and Orville-Thomas<sup>298</sup> between 5000 cm<sup>-1</sup> and 450 cm<sup>-1</sup>. The results indicate that the molecule is planar.

The far infrared spectrum of an etherified melamine-formaldehyde resin (Figure 111) similar to that of a urea-formaldehyde resin, shows only one broad and intense band with its maximum around 630 cm<sup>-1</sup>. At least two vibrational modes contribute to this band, an in-plane bending of the triazine ring, and a C-O-C bending vibration of the ether groups. An oil-modified melamine resin showed an additional absorption from the vegetable oil at about 450 cm<sup>-1</sup> (Figure 112).

Benzoguanamine resins are often used in combinations with other amino- or amido formaldehyde resins and alkyd resins. The far infrared spectrum (Figure 113) is characterized by a strong, asymmetric band with its maximum at 645 cm<sup>-1</sup> and two weaker, but rather sharp bands at 460 cm<sup>-1</sup> and 320 cm<sup>-1</sup>.

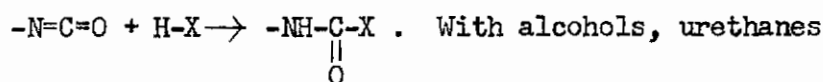
Sulfonamide-formaldehyde resins are less common than the other resins described above. Best known are the toluene sulfonamide resins. The far infrared spectrum of a resin of this type (Figure 114) is very pronounced by strong bands at 660, 590, and 545 cm<sup>-1</sup>, caused by deformation vibrations of this group:



The infrared spectra of some sulfonamides between 4000 cm<sup>-1</sup> and 400 cm<sup>-1</sup> were studied by Baxter et al.<sup>299</sup>

### 3. Other Nitrogen Containing Resins and Polymers

a. Polyurethanes and Isocyanates. Isocyanates react with active hydrogen atoms according to the following mechanism:



are formed as follows:  $-N=C=O + ROH \rightarrow -NH-CO-OR$ . Polyurethanes are formed by using di or polyfunctional isocyanates and alcohols. The reactions of isocyanates were extensively studied by Bayer<sup>300-302</sup> and later found tremendous industrial application.

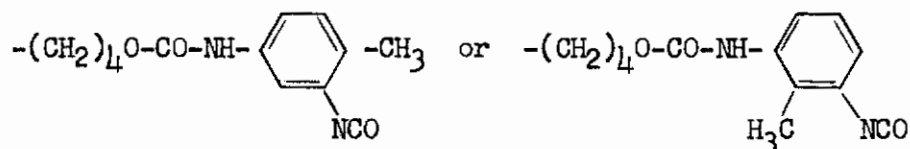
Most of the industrially important polyurethanes, contrary to the polyesters or polyamides, do not contain the characteristic group in regular sequences. The di- or triisocyanates are used principally as connecting links between long chain polyesters or polyethers with hydroxyl end groups. Thus the specific properties of the urethane group do not determine the properties of the polymer compound.

Polyurethanes with  $-NH-CO-O-$  as a characteristic group should exhibit spectral similarities to amides as well as esters. This is true for the rock-salt range where the carbonyl band found in urethanes absorbs near  $1724 \text{ cm}^{-1}$  and the amide II band at  $1540 \text{ cm}^{-1}$ . In the far infrared a characteristic absorption band probably arising from an out-of-plane deformation vibration of the associated NH-group often appears between  $600 \text{ cm}^{-1}$  and  $650 \text{ cm}^{-1}$ .

"Durethan U<sub>0</sub>" is an aliphatic polyurethane from hexamethylene diisocyanate and butanediol-1,4. It is exceptional in having a regular sequence of urethane groups and being based on an aliphatic isocyanate. The strongest band in its far infrared spectrum (Figure 115) has its maximum at  $640 \text{ cm}^{-1}$ . The band is rather broad and due to this fact and its wavenumber position, it resembles the amide band V of secondary amides.

# Conclusions

The Adiprenes L-100 and L-167 are polytetrahydrofuranes which were reacted with a mixture of the isomeric toluene diisocyanates. Thus the end groups in the adiprenes have the following structures:



If the assignment stated above is correct, then the absorption at about  $630 \text{ cm}^{-1}$  in the spectra of the adiprenes (Figures 116 and 117) is due to the urethane groups. A similar band occurs at  $620 \text{ cm}^{-1}$  in the spectrum of "Desmodur TT stabil" (Figure 118), which is a phenylurethane of the dimerized toluene-2,4-diisocyanate. It is dubious whether the band at  $613 \text{ cm}^{-1}$  in the spectrum of "Desmodur AP stabil" (Figure 119) has the same origin. This resin is a phenylurethane of a reaction product of one mole hexanetriol and three moles toluene-diisocyanate.

The infrared absorptions of the isocyanate group were studied by a few authors.<sup>303-305</sup> The far infrared absorptions of this group are uncertain. There should be at least one fairly strong bending vibration of this type:  $\begin{matrix} \uparrow \\ -\text{C}-\text{NCO} \\ \downarrow \end{matrix}$ . This vibration probably mixes with bending vibrations of the adjacent groups. All of the molecules containing isocyanate groups, studied by us (Figures 116-120), exhibited a fairly strong band between  $550 \text{ cm}^{-1}$  and  $565 \text{ cm}^{-1}$  and a medium but sharp band near  $440 \text{ cm}^{-1}$ . One of these may tentatively be assigned to the bending vibration shown above.

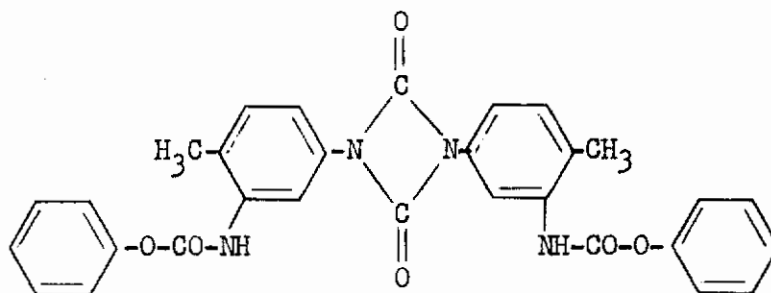


The Adiprenes have the strongest bands at  $560 \text{ cm}^{-1}$  and  $445 \text{ cm}^{-1}$ . At least

# Contrails

the former partly stems from the ether linkages in the polytetrahydrofuran chain. "Desmodur TT stabil" has similar bands at  $555\text{ cm}^{-1}$  and  $445\text{ cm}^{-1}$ .

Its structure is:



Further work is necessary to find out if this pair of bands is characteristic for the isocyanate group, whether monomeric or dimeric, or if it is related to the 1,2,4-substituted ring systems.

b. Polyacrylonitrile. For industrial purposes acrylonitrile is usually copolymerized with small amounts of other comonomers like vinyl acetate or acrylic acid. On the other hand, certain plastics like high-impact polystyrenes, and synthetic rubbers like the "Buna N" type butadiene copolymers contain smaller or larger amounts of acrylonitrile units in their chains.

The infrared spectrum of polyacrylonitrile was studied by a number of authors.<sup>306-308</sup> Liang and Krimm<sup>306</sup> gave a rather complete assignment of the bands between  $3200\text{ cm}^{-1}$  and  $70\text{ cm}^{-1}$ . Table 27 shows their results for the bands below  $700\text{ cm}^{-1}$ .

The far infrared spectrum of a copolymer with about 6% vinyl acetate (Figure 121) shows, in addition to the bands of polyacrylonitrile, absorptions near  $603\text{ cm}^{-1}$  and  $630\text{ cm}^{-1}$  belonging to vibrations of the vinyl acetate units.



TABLE 27

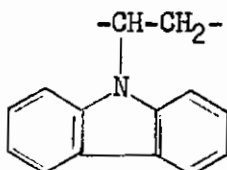
Far Infrared Absorption Bands of Polyacrylonitrile

According to Liang and Krimm<sup>306</sup>

<u>Wavenumber, cm<sup>-1</sup></u>	<u>Intensity</u>	<u>Dichroic Behavior</u>	<u>Assignment</u>
675	w	-	Combination vibration
532	m	$\perp$	$\delta$ (C-CN)
430	w	$\perp$	$\delta$ (CN)
259	ms	Not determined	$\gamma_w$ (C-CN)
127	vs	Not determined	$\gamma_w$ (CN)
86	mw	Not determined	Subtraction vibration

Yamadera<sup>307</sup> described an infrared spectroscopic method for the determination of end groups in polyacrylonitrile. Bayzer and Schurz<sup>308</sup> investigated the saponification products of polyacrylonitrile and of vinyl chloride-acrylonitrile copolymers.

c. Polyvinylcarbazole. Polyvinylcarbazole has the monomer unit



and is a very hard and high-melting resin. It has outstand-

ing dielectrical properties and is used in surface coatings.

Its far infrared spectrum (Figure 122) is characterized by a number of pronounced bands. The one at  $530\text{ cm}^{-1}$  is probably an in-plane bending vibration of the o-substituted rings. A fairly strong band near  $420\text{ cm}^{-1}$  is probably caused by an out-of-plane ring bending vibration involving the nitrogen atom.

## J. Silicones

The name "silicone" is derived from "ketone" since both have analogous general formulas:  $\text{R-CO-R}'$  and  $(\text{R-SiO-R}')_n$ . However, Si is not able to form double bonds, and therefore the term "polysiloxanes" is more correct.

The most commonly used silicones are the polydimethylsiloxane and the polymethylphenylsiloxane. The former is the main constituent in silicone rubbers, the latter is often found in resin combinations for high-temperature surface coatings.

The infrared spectra of polysiloxanes and similar silicon compounds were extensively studied.<sup>309-320</sup> Generally, vibrations involving chemical groups with silicon are about five times as strong as those of similar groups with carbon. This is also true for the far infrared where the bending vibrations

of the siloxane chain and of the substituents cause extremely strong bands.

The far infrared spectrum of polydimethylsiloxane (Figure 123) is comparably simple but very characteristic. Two very strong bands near  $475\text{ cm}^{-1}$  and  $385\text{ cm}^{-1}$  dominate the spectrum. They are very likely caused by a Si-O-Si bending, and by an O-Si-CH<sub>3</sub> bending vibration, respectively. The band near  $275\text{ cm}^{-1}$  may be due to a methyl twisting vibration.

Similar bands, though with reversed intensity, are found in the far infrared spectrum of a polymethylphenylsiloxane (Figure 124). The band near  $605\text{ cm}^{-1}$  probably belongs to an in-plane bending vibration; the one near  $440\text{ cm}^{-1}$  to an out-of-plane bending vibration of the monosubstituted ring. The latter apparently couples with a skeleton vibration of the siloxane chain; this would explain its intensity.

Harvey and Nebergall<sup>319</sup> assigned a strong band near  $515\text{ cm}^{-1}$  in the spectra of compounds with the C<sub>6</sub>H<sub>5</sub>-Si-C<sub>6</sub>H<sub>5</sub> group to the asymmetric stretching vibration of the group C-Si-C. For methyl phenyl siloxanes, we would prefer to assign tentatively the sharp and strong band at  $665\text{ cm}^{-1}$  to an Si-phenyl stretching vibration and a band near  $540\text{ cm}^{-1}$  to an O-Si-phenyl bending vibration.

## K. Waxes and Asphalts

Aliphatic asphalts do not significantly absorb in the far infrared (Figure 125). Montan wax is a mineral wax which contains long chain fatty acids and high molecular weight aliphatic esters. The strongest band at  $540\text{ cm}^{-1}$  in the far infrared spectrum (Figure 126) belongs to a bending vibration of the C-CO-O grouping. Beeswax is a mixture of myricyl palmitate, long chain fatty acids and small amounts of other compounds. The far infrared spectrum of the liquid (not shown) exhibits three very broad absorptions

belonging to deformation vibrations of the ester and carboxylic groups. The spectrum of the crystalline wax (Figure 27) shows numerous absorption bands. The maxima at 580, 540, 430, and 400  $\text{cm}^{-1}$  are best suited for identification. Carnauba wax is a palm wax consisting mainly of high molecular weight hydrocarbons, higher alcohols and their esters and small amounts of other compounds. The far infrared spectrum (Figure 128) is sufficiently characteristic for an identification. The strongest band at 515  $\text{cm}^{-1}$  belongs to the bending vibration of the ester and carbonyl groups. Candelilla wax is obtained from certain shrubs in Mexico and Japan. Chemically, it is a mixture of high molecular weight hydrocarbons and ester and acid resins. It is rather unsaturated. Its far infrared spectrum (Figure 129) shows some similarities to the spectrum of Montan wax (Figure 126). However, the absorptivity of the strongest band at 545  $\text{cm}^{-1}$  is about three times lower in Candelilla wax due to its content of hydrocarbons.

Generally, both natural and synthetic waxes may readily be identified by their far infrared spectra.

## L. Plasticizers

### 1. Aliphatic Esters of Carboxylic Acids.

The far infrared spectra of higher aliphatic esters are rather uncharacteristic in showing only the absorptions of the ester group. Consequently, aliphatic ester-type plasticizers cannot be easily identified by their far infrared spectra. The main absorptions in the spectra of diethylhexyladipate (Figure 130) and diethylhexylsebacate (Figure 131) were at 580, 480, and about 300  $\text{cm}^{-1}$ .

### 2. Phthalates (Chart IX)

Esters of the o-phthalic acid have altogether four characteristic

# Contraails

absorptions in the far infrared. The first, with one exception, is always found at exactly  $650\text{ cm}^{-1}$ . Since it is very sharp and usually has no surrounding bands, it can be used for quantitative determinations. Only in the case of phenolic esters of the phthalic acid, the conjugated  $\pi$ -electron system produces a slight shift of this absorption from  $650\text{ cm}^{-1}$  to about  $655\text{ cm}^{-1}$ . The second, and also rather strong band occurs in the wider range between  $560\text{ cm}^{-1}$  and  $590\text{ cm}^{-1}$ . The third band is usually found around  $400\text{ cm}^{-1}$  and partially fused with a very broad and strong band between  $330\text{ cm}^{-1}$  and  $360\text{ cm}^{-1}$ . The other bands in the spectra of phthalate plasticizers (Figures 132-147) serve as "finger-print bands" for the identification of the individual compounds.

The assignment of the bands at  $650\text{ cm}^{-1}$  and between  $560\text{ cm}^{-1}$  and  $590\text{ cm}^{-1}$  is not clear. The in-plane bending vibration of ortho-disubstituted benzene derivatives was found between  $495\text{ cm}^{-1}$  and  $555\text{ cm}^{-1}$  as a weak to medium band. The infrared active out-of-plane ring deformation vibration was found between  $418\text{ cm}^{-1}$  and  $470\text{ cm}^{-1}$  as a medium to strong band.<sup>110</sup> On the other hand, the asymmetric bending vibration of the ester group is sometimes found as high as  $650\text{ cm}^{-1}$ . This strongly suggests the band at  $650\text{ cm}^{-1}$  to be an ester bending vibration. However, this vibration is known to be very sensitive to the kind of substituent, and this band in the phthalates apparently is not. Furthermore, the other band between  $560\text{ cm}^{-1}$  and  $590\text{ cm}^{-1}$  varies its maximum with the kind of substituent and is well in the range of a bending vibration of the ester group.

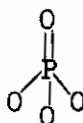
It is a likely assumption that the two carbonyl groups being conjugated to the benzene ring alter the ranges of the ring vibrations considerably. Actually, no band in the range for the out-of-plane ring deformation vibration ( $470\text{-}418\text{ cm}^{-1}$ ) could be found. We should, therefore, prefer to consider the

band at  $650\text{ cm}^{-1}$  as a vibration of the aromatic system, and the next one as an ester vibration. The band near  $350\text{ cm}^{-1}$  is probably an out-of-plane vibration of the ester group. Further assignments were not tried.

### 3. Phosphates (Chart X)

The infrared spectra of phosphoric acid esters and similar compounds were studied by a large number of authors.<sup>321-329</sup> Owing to the strong polarity of the phosphate group, its stretching and deformation vibrations give rise to intense absorptions both in the rocksalt range and in the far infrared.

Table 28 shows the far infrared absorptions of some phosphoric acid esters between  $700\text{ cm}^{-1}$  and  $250\text{ cm}^{-1}$ , found by Mortimer<sup>327</sup> and in our study. As to the assignments, it may be helpful first to consider the phosphate group as an isolated unit:



. This should exhibit two infrared

active bending vibrations; a symmetric one and an asymmetric one (compare the bending vibrations of a methyl group). These bending vibrations should give rise to rather strong infrared bands. If alkyl groups are attached to the three single-bonded oxygen atoms the C-O bending vibrations will appear in the spectrum, but will be coupled with the P-O bending vibrations.

Actually, the spectra of alkylphosphates show two strong bands between  $525\text{ cm}^{-1}$  and  $560\text{ cm}^{-1}$  and between about  $400\text{ cm}^{-1}$  and  $460\text{ cm}^{-1}$ . Their position in the spectrum is very sensitive to the kind of substituent. Other bands, partially fused with the ones mentioned above, occur in the same range but are somewhat weaker. They are also sensitive to the kind of substituent. This clearly shows that we have a set of mixed vibrations involving both bending of the  $\text{PO}_3$  angles and bending of the C-O-P angles.

TABLE 28

Far Infrared Absorptions of Some Liquid Phosphoric Acid Esters

Between 700 and 250  $\text{cm}^{-1}$

Trimethylphosphate <sup>1</sup>	Triethylphosphate <sup>1</sup>	Tri-n-butylphosphate <sup>2</sup>	Triphenylphosphate	
(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	1	2
			687	688
			620	660
			579	578
526	545	557 + 540 (sh) <sup>3</sup>	565	565(sh) <sup>3</sup>
500	525	510	518	518
			497	495-505
459	465	463	470	460 (sh) <sup>3</sup>
		425		
		363		
		275		

1 Mortimer<sup>327</sup>

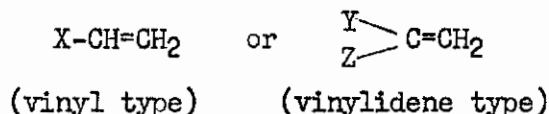
2 This Report

3 sh = shoulder

Crystallization causes considerable changes in the far infrared spectrum of phosphoric acid esters.<sup>327</sup> The ones shown in this report (Figures 148-156) were all in the liquid state.

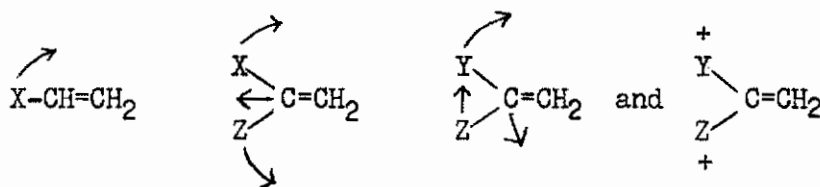
## M. Monomers (Chart XI)

Olefin-type monomers usually have one of the two following general structures:



Both the vinyl and the vinylidene group have very significant absorptions in the rocksalt range caused by the C=C stretching and the out-of-plane deformation vibrations of the hydrogen atoms attached to the olefinic double bond.

In the far infrared we may expect a torsional vibration of the =CH<sub>2</sub> group, and deformation vibrations of the substituents X, Y, or Z of the following types:



Bentley and Wolfarth<sup>19</sup> found the following absorptions of different alkenes in the far infrared (see Table 29). Harrah and Mayo<sup>330</sup> later found that all 1-alkenes, with the exception of propene, exhibit two medium infrared bands near 630 cm<sup>-1</sup> and 550 cm<sup>-1</sup>. Both bands are caused by a vibration of the vinyl group, probably the torsional vibration of the =CH<sub>2</sub> group. It is very likely that the band near 550 cm<sup>-1</sup> belongs to an almost planar conformation of the vinyl group with the C<sub>2</sub>-C<sub>4</sub> plane. The band near 630 cm<sup>-1</sup> probably belongs to the more stable conformation where the vinyl group is



TABLE 29

Far Infrared Absorptions of Alkenes

According to Bentley and Wolfarth<sup>19</sup>

<u>Unbranched</u>	<u>1-Alkenes</u>		<u>cis-2-Alkenes</u>	<u>trans-2-Alkenes</u>
	<u>α-Branched</u>	<u>Remote Branch</u>		
(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
637-629		625-614	588-571	417-385
554-549	559-532		488-465	323-286

# Conclusions

rotated around the C<sub>2</sub>-C<sub>3</sub> bond by angles of  $\pm 30^\circ$  or  $\pm 90^\circ$ . Apparently branching of the alkyl chain may favor one or the other conformation, as suggested by the results of Bentley and Wolfarth.<sup>19</sup>

The in-plane bending vibration of the C-C-X group (X = C or O) was found for propylene<sup>331</sup> near 417 cm<sup>-1</sup>, for butene-1<sup>332</sup> near 437 cm<sup>-1</sup>, and for vinyl ethers<sup>333</sup> between 421 cm<sup>-1</sup> and 478 cm<sup>-1</sup>, depending on the conformation of the molecule.

Most of the olefin-type monomers studied in this report exhibit a band between about 375 cm<sup>-1</sup> and 430 cm<sup>-1</sup> in their far infrared spectra (Figures 158-174). The intensity is varying from weak to strong depending upon the substituents. We assign this band tentatively to the C-C=C in-plane bending vibration.

Vinylidene-type monomers with the general structure:

$$\begin{array}{c} \text{Y} \\ \diagdown \\ \text{C} = \text{CH}_2 \\ \diagup \\ \text{Z} \end{array}$$

usually exhibit a medium band between 505 cm<sup>-1</sup> and 540 cm<sup>-1</sup>. It is not unlikely that this band is caused by the asymmetric, degenerate in-plane bending vibration of the C $\begin{array}{c} \text{Y} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{Z} \end{array}$  group. However, neither the assignment nor the range given here can be considered as final, especially since this vibration, in its nature and its frequency, depends upon the nature of the substituents.

Aromatic monomers (Figures 160-162) show additional bands due to deformation vibrations of the aromatic ring system.

Ester type monomers display absorptions of the ester group around 650 cm<sup>-1</sup> and 350 cm<sup>-1</sup>. In addition to these, methacrylates are well characterized by a doublet at 590 cm<sup>-1</sup> and 600 cm<sup>-1</sup> probably arising from the  $\alpha$ -methyl group.

## N. Solvents

The spectra (Figures 175-192) show a number of substances which are frequently used as solvents for polymers and resins, or as dispersants for mulls (paraffin oil). Since small amounts of the solvent frequently cannot be removed from the polymer even by long drying in a vacuum oven, it is very important to know where the strongest bands of the solvent may occur in the spectrum. In some cases, the polymer may interact with the remaining solvent molecules in a way that small shifts in the band maximum, and also changes in the absorptivity of the bands occur.

Chloroform is a very good solvent for many polymers and resins. Unfortunately, it often sticks tenaciously in the sample and adulterates the spectrum with its strong or medium bands at 667, 625, and 365  $\text{cm}^{-1}$  (Figure 178). Since methylene chloride is also an excellent solvent and does not absorb too much in these ranges (Figure 177), it is sometimes advisable to make use of this solvent. Evaporation of methylene chloride from the film should not be performed too rapidly because water will then condense and spoil the film.

A very reasonable solvent for the far infrared is benzene (Figure 190) since it has only one weak absorption at 395  $\text{cm}^{-1}$  in the range between 600 and 300  $\text{cm}^{-1}$ . Rather universal solvents are dimethyl sulfoxide (Figure 188) and dimethylformamide (Figure 189). Both do not absorb between about 650  $\text{cm}^{-1}$  and 400  $\text{cm}^{-1}$ . Due to the similarity in structure the spectra are also rather similar.

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APPENDICES

INFRARED SPECTRA AND  
CORRELATION CHARTS

APPENDIX A

COLLECTION OF SPECTRA OF  
HIGH POLYMERS, RESINS, AND RELATED SUBSTANCES  
IN THE 700-250  $\text{cm}^{-1}$  REGION

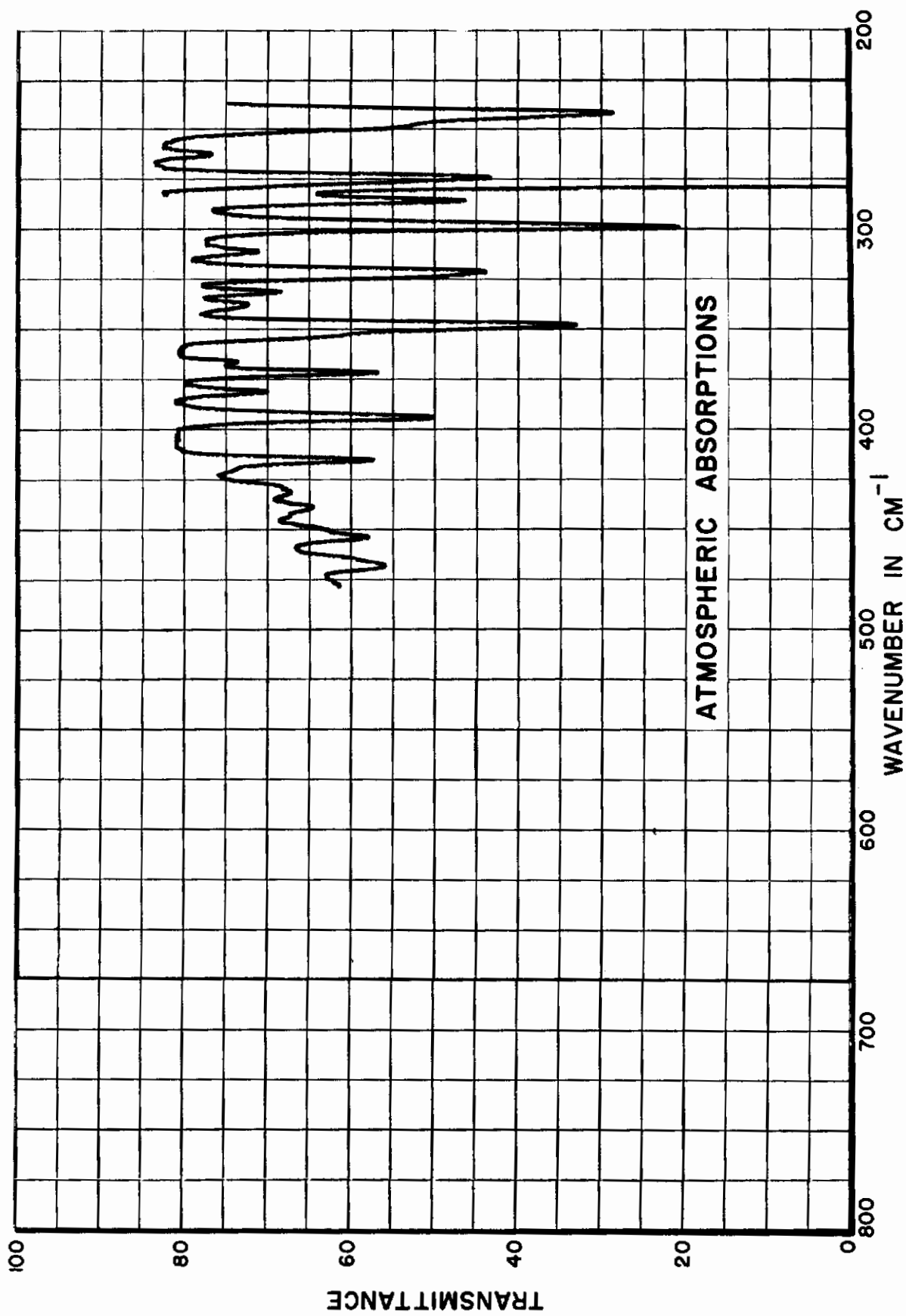


Figure 1. - Infrared Spectrum from 500 - 250 cm<sup>-1</sup> of Water Vapor

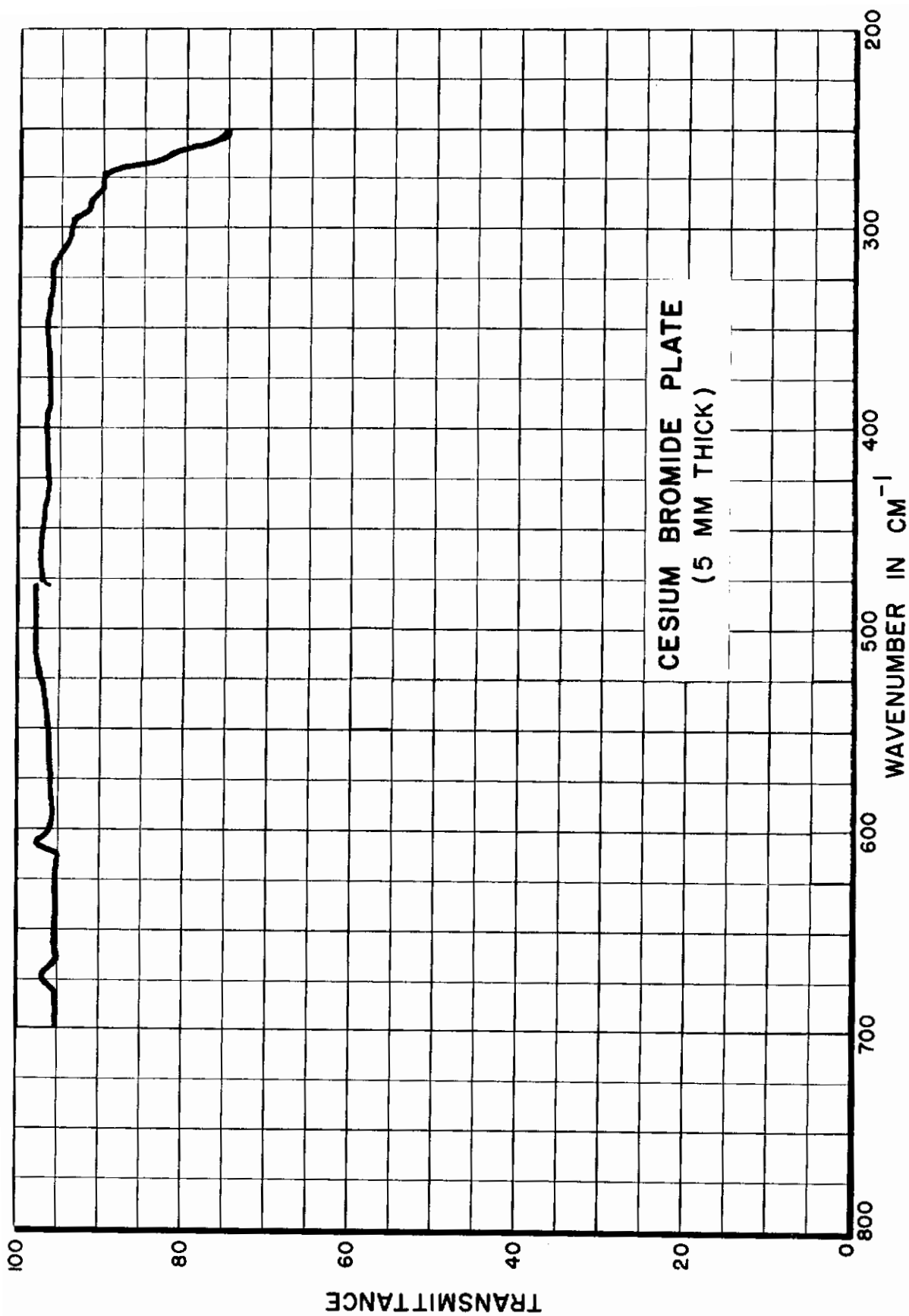


Figure 2. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of a Cesium Bromide Plate

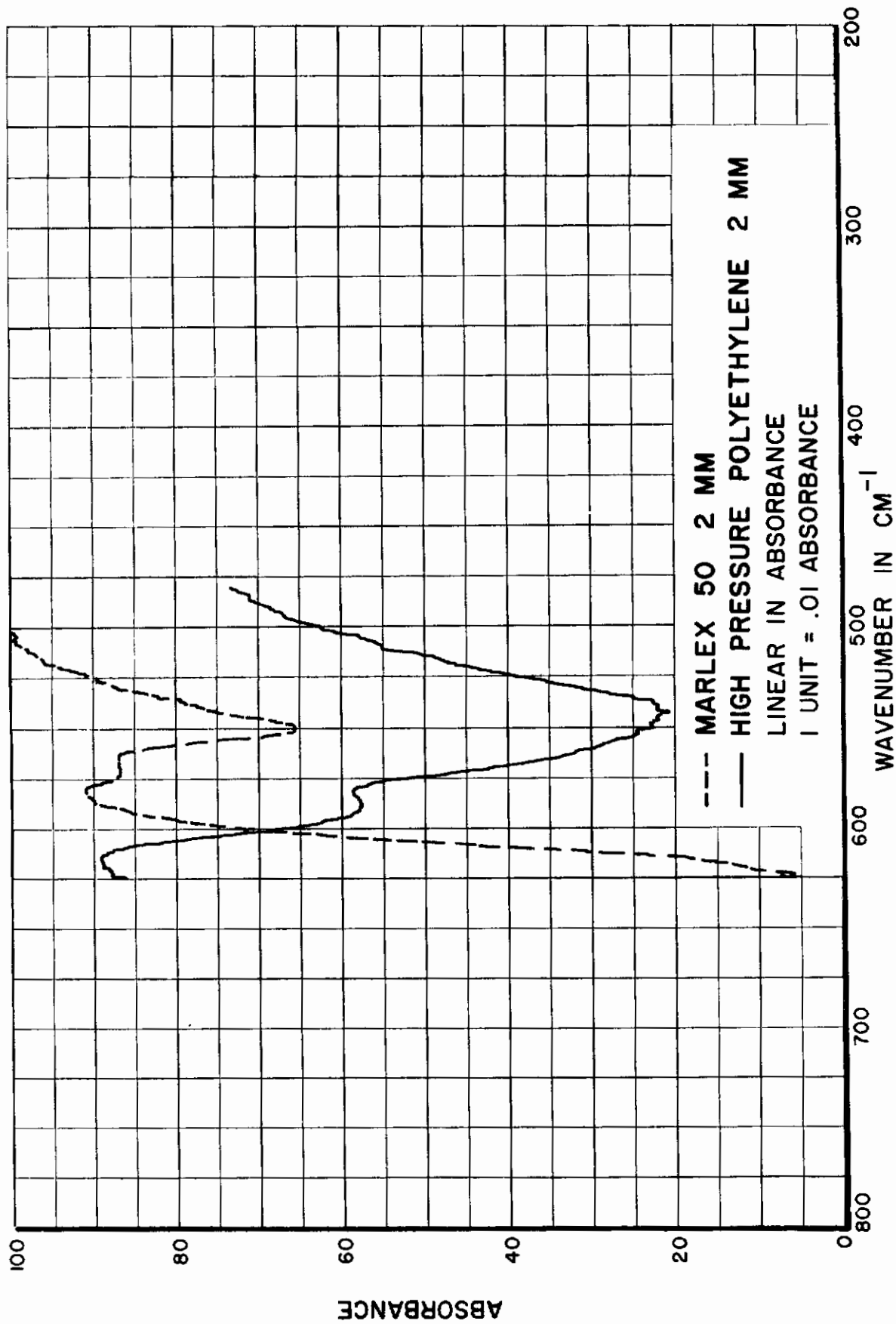


Figure 3. - Infrared Spectra from 625 - 500 cm<sup>-1</sup> of Marlex 50 (Linear Polyethylene) and High Pressure Polyethylene (Branched)  
Recorded as pressed sheets



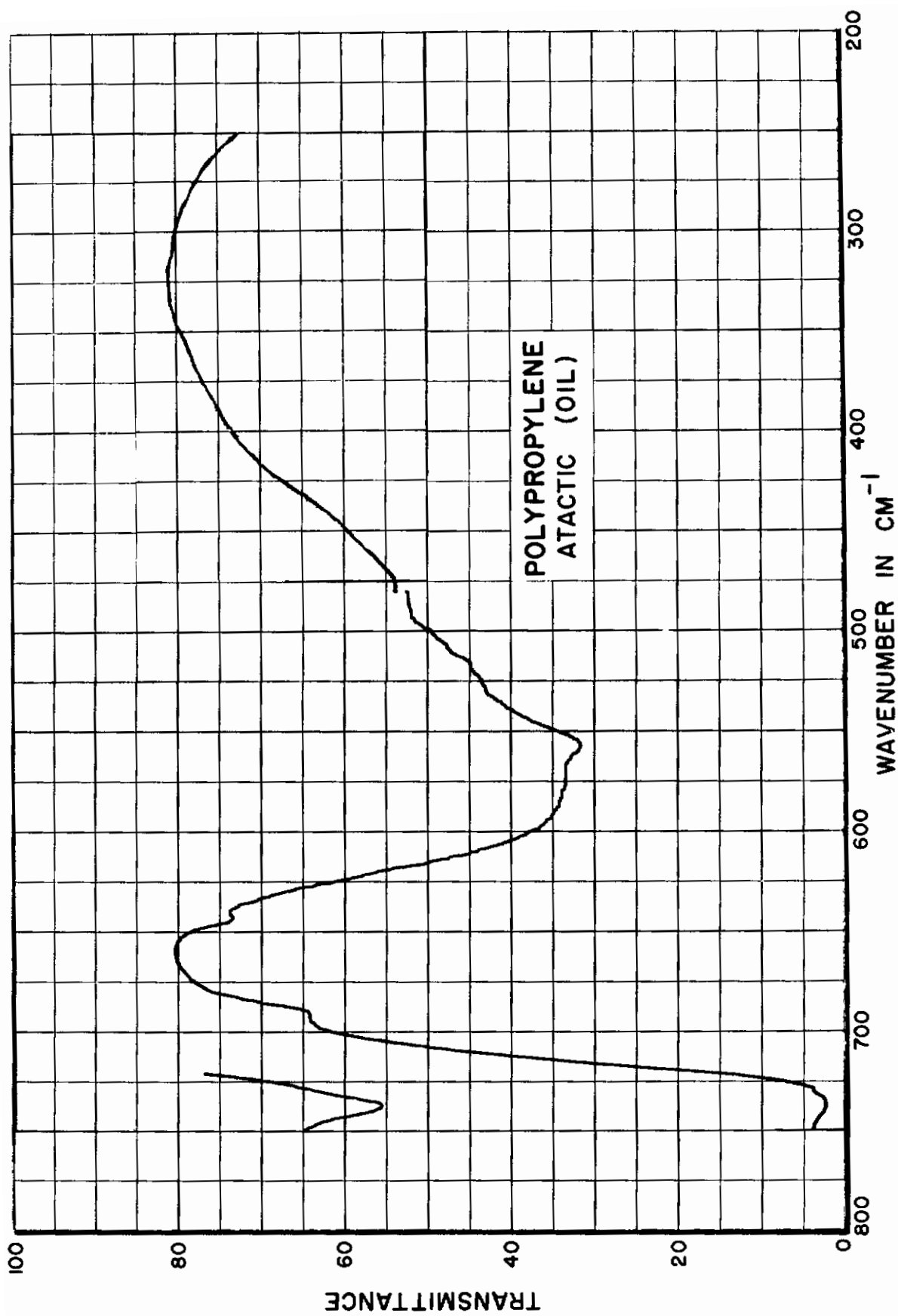


Figure 4. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Polypropylene (Low Molecular Weight Oil)  
Recorded as a film

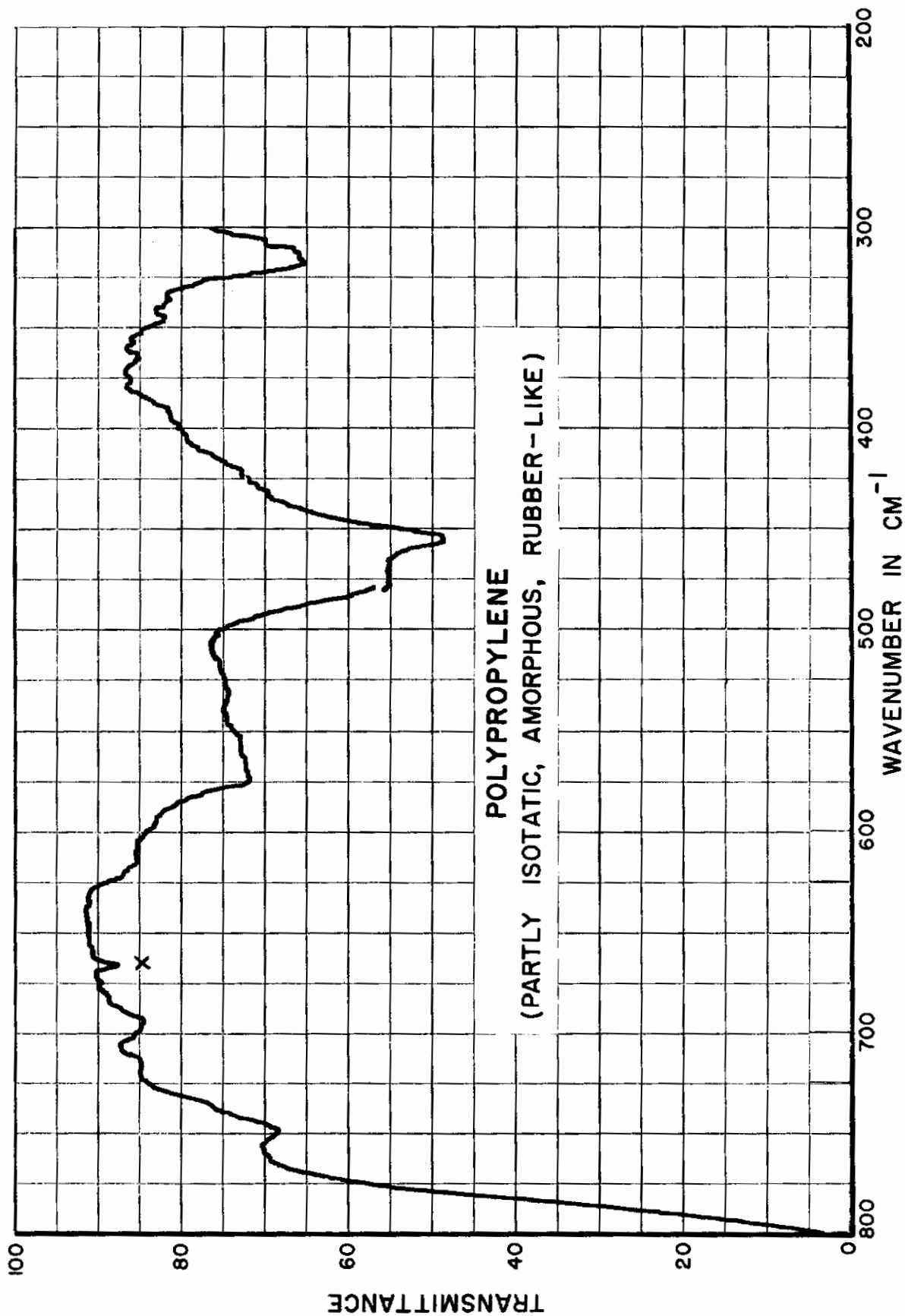


Figure 5. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Polypropylene (Partly Isotactic, Amorphous and Rubber-like)

Recorded as a pressed sheet

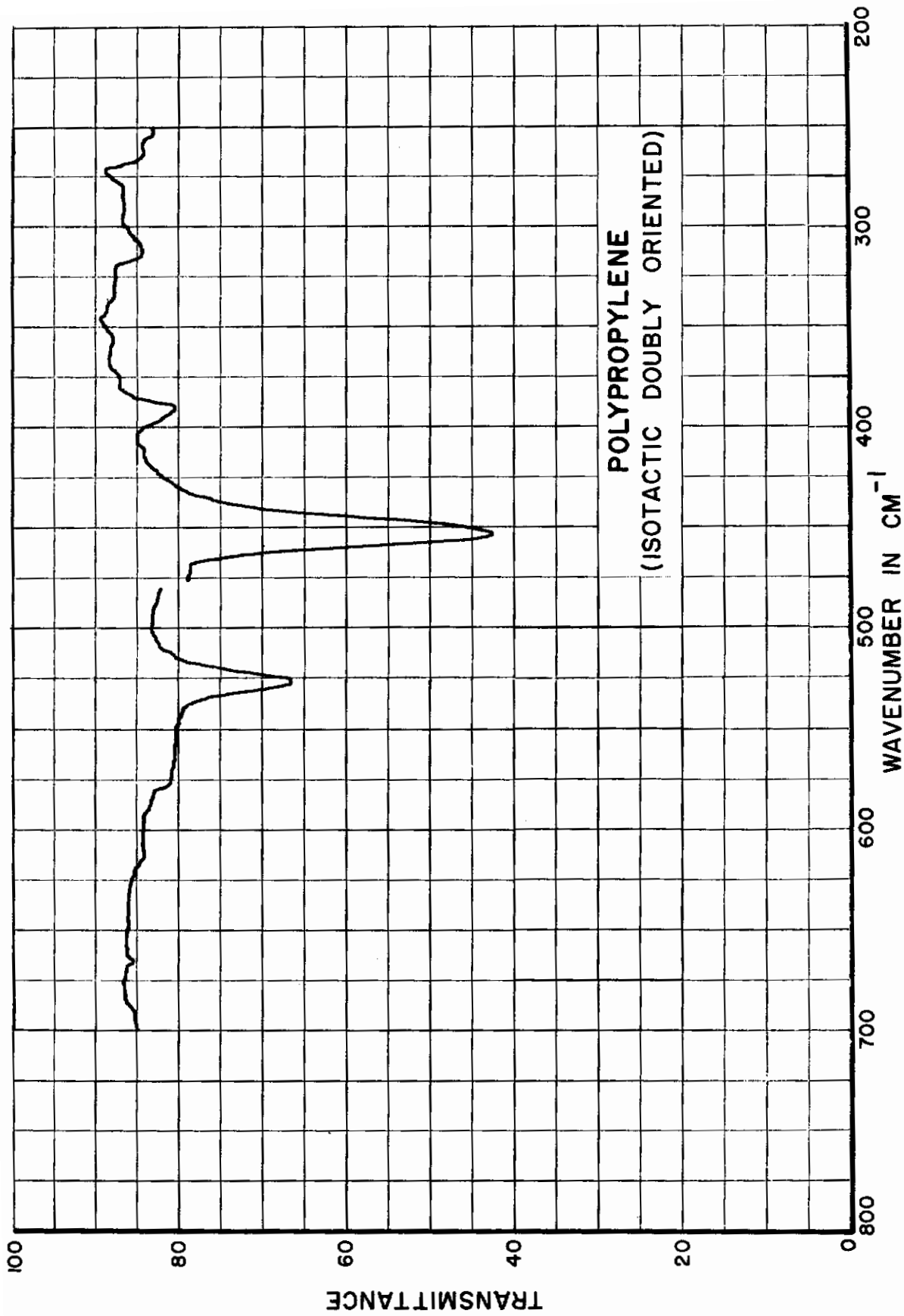


Figure 6. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Polypropylene (Isotactic, Crystalline and Biaxially Oriented)  
Recorded as a film, 0.32 mm in thickness

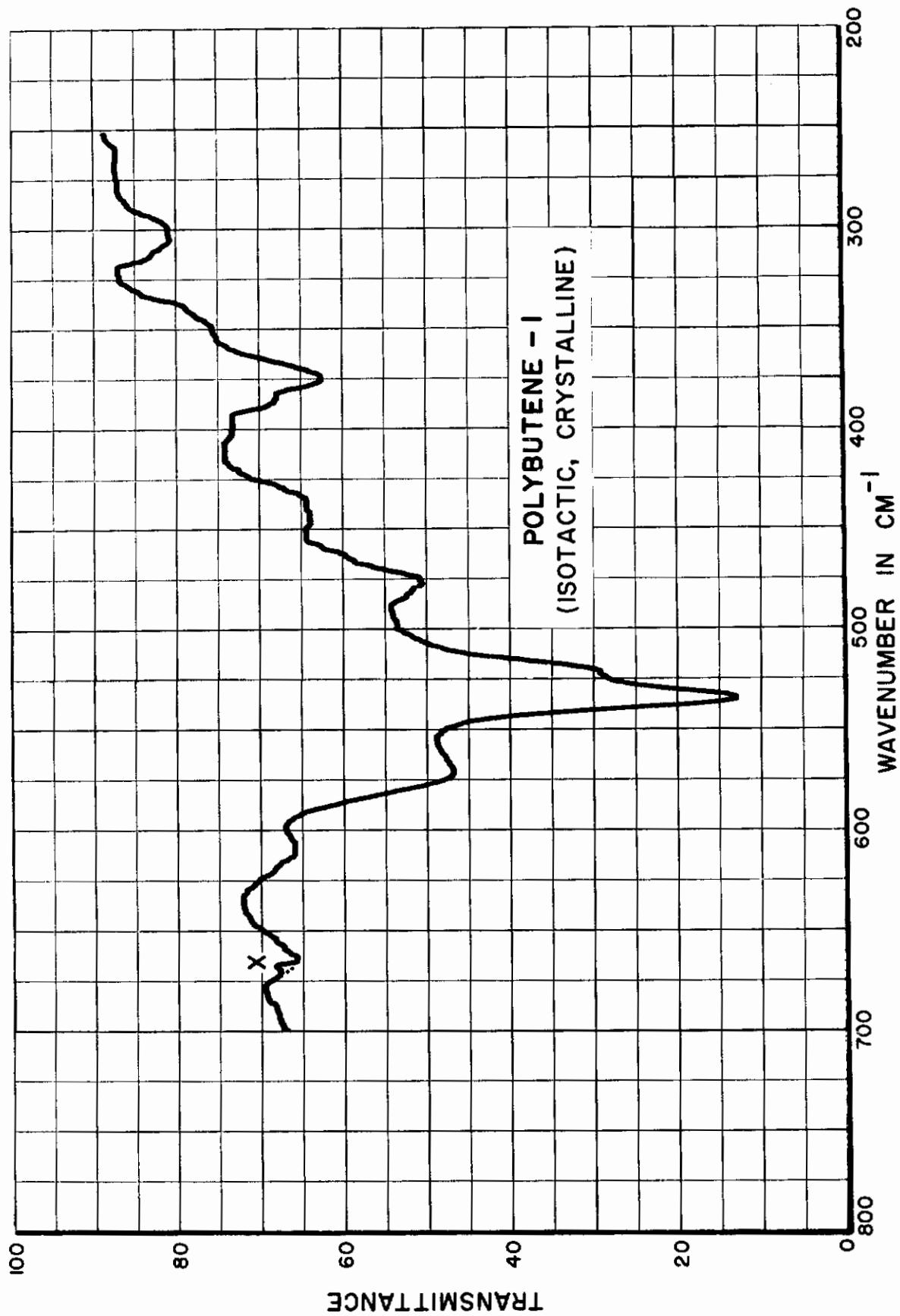


Figure 7. - Infrared spectrum from 700 - 250 cm<sup>-1</sup> of Polybutene-1 (Isotactic and Crystalline)  
Recorded as a pressed film approximately 0.6 mm in thickness

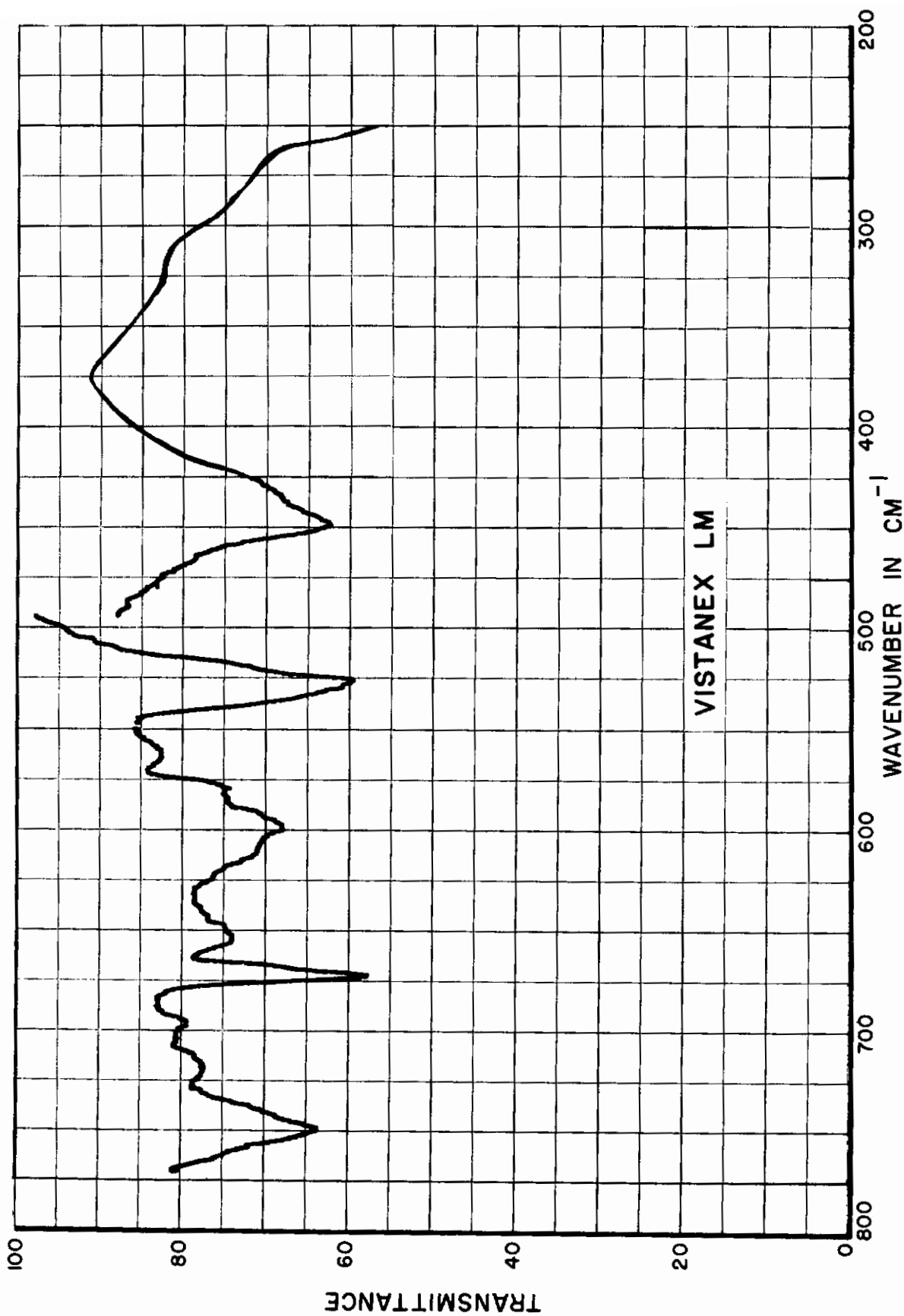


Figure 8. - Infrared Spectrum from 875 - 250 cm<sup>-1</sup> of Vistanex LM (Polyisobutylene)  
Recorded as a film

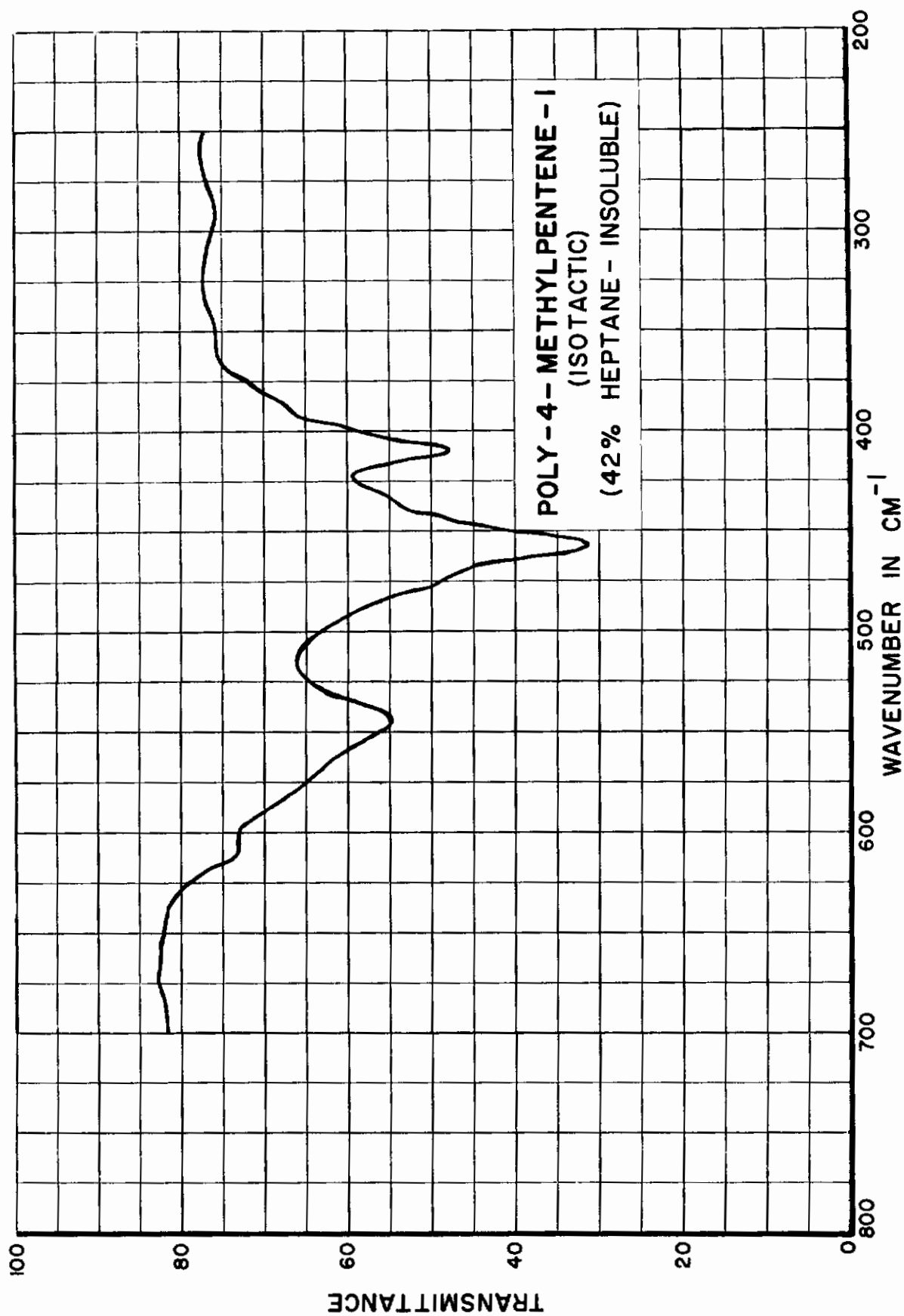


Figure 9. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Poly-4-Methylpentene-1 (Isotactic and Crystalline)  
Recorded as a Nujol mull

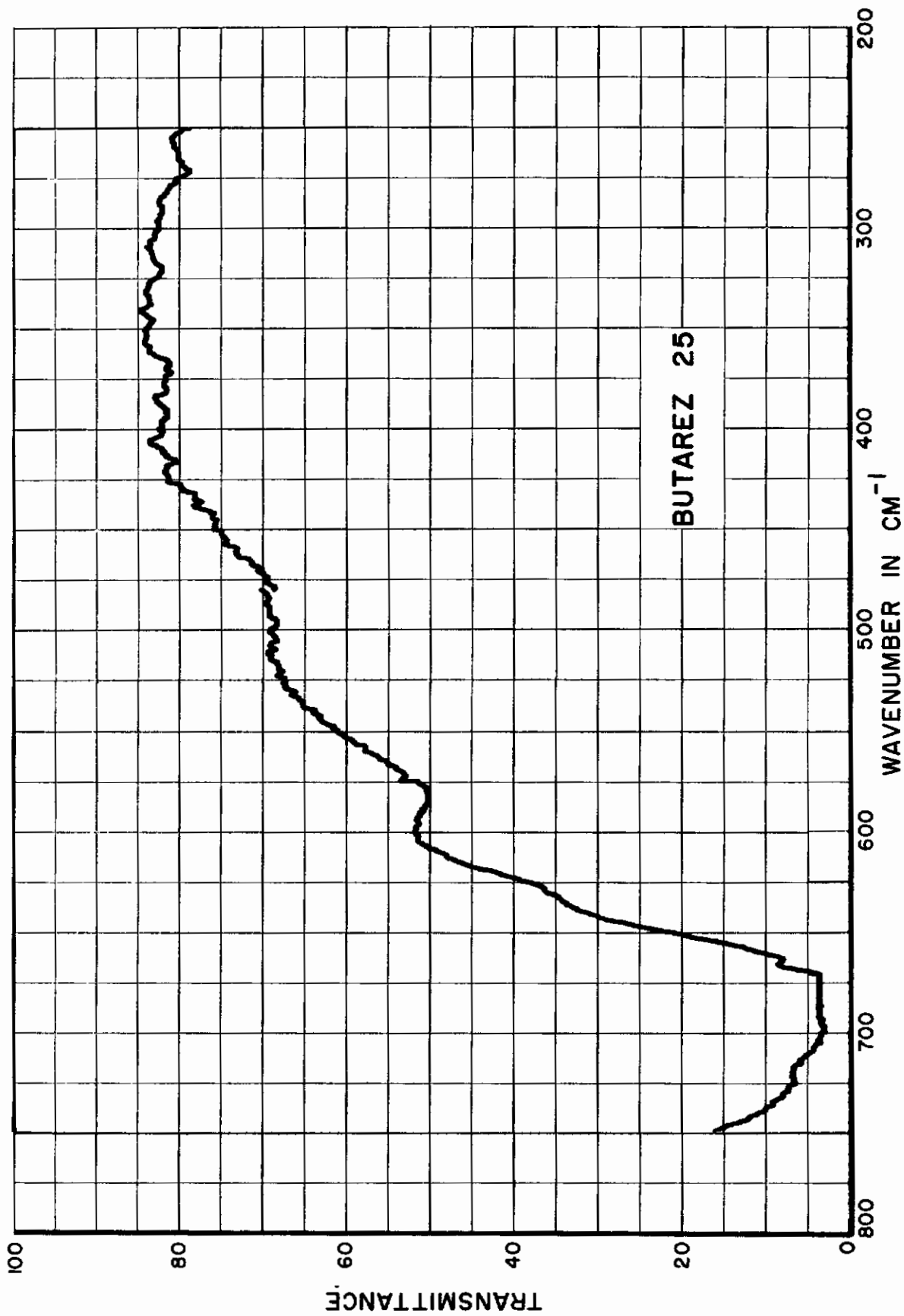


Figure 10. - Infrared Spectrum from 750 - 250  $\text{cm}^{-1}$  of Butarez 25 (Atactic Polybutadiene in Liquid State)

Recorded as a capillary film

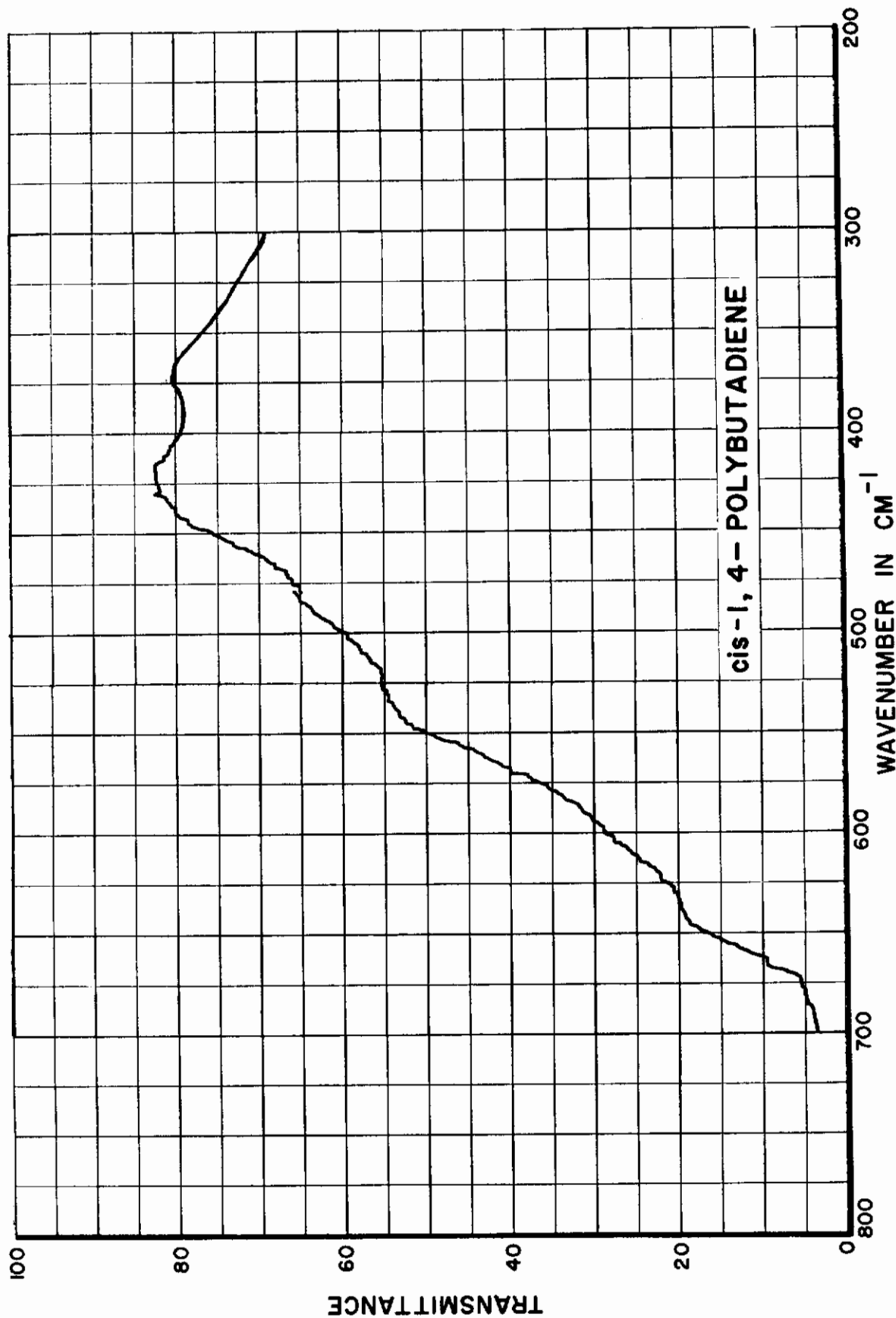


Figure 11. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of cis 1,4-Polybutadiene (Small Amounts of Other Structures also Present)  
Recorded as a film from chloroform solution



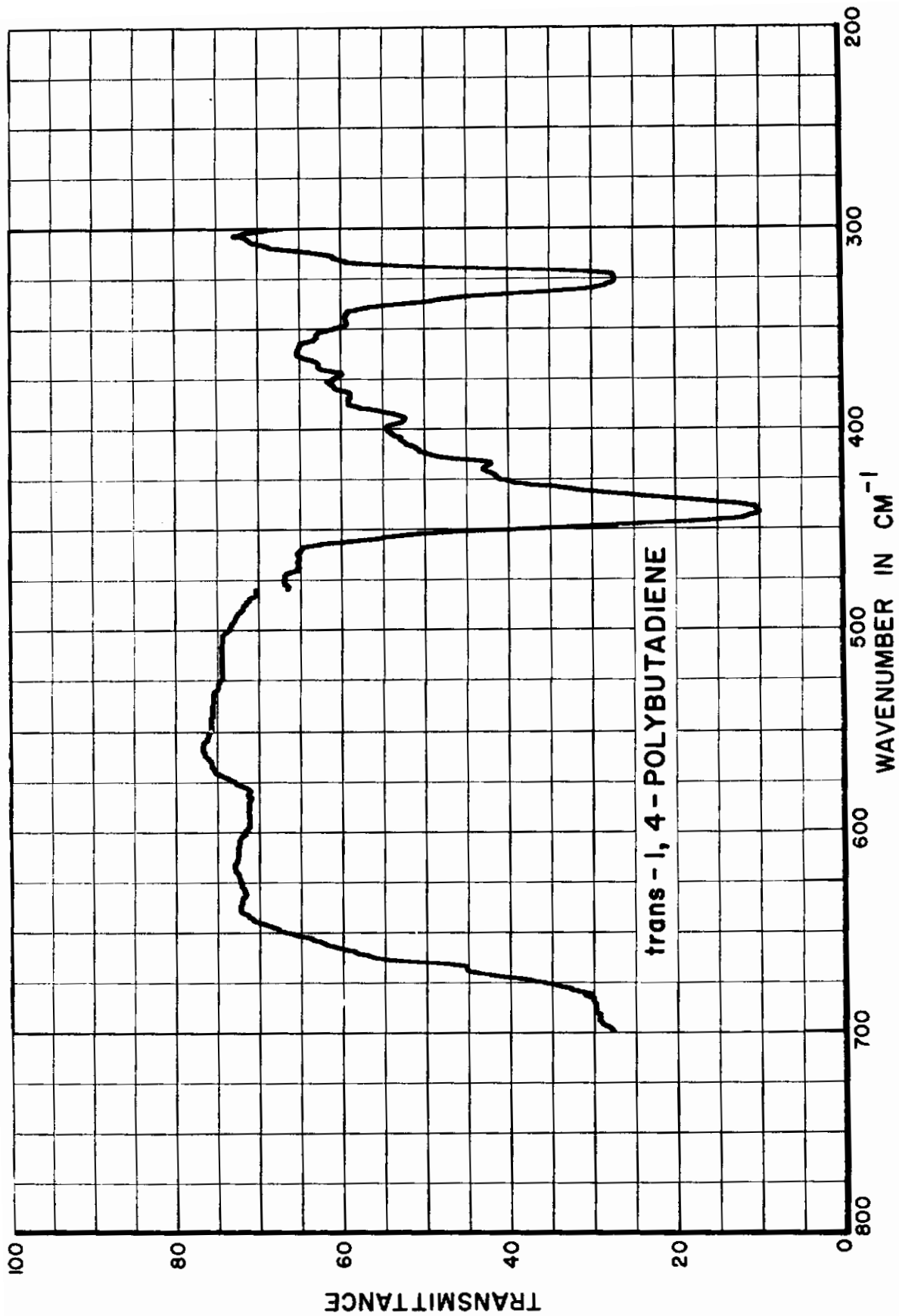


Figure 12. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of trans 1,4-Polybutadiene (Small Amounts of Other Structures also Present)

Recorded as a film approximately 0.25 mm in thickness, prepared from a chloroform solution

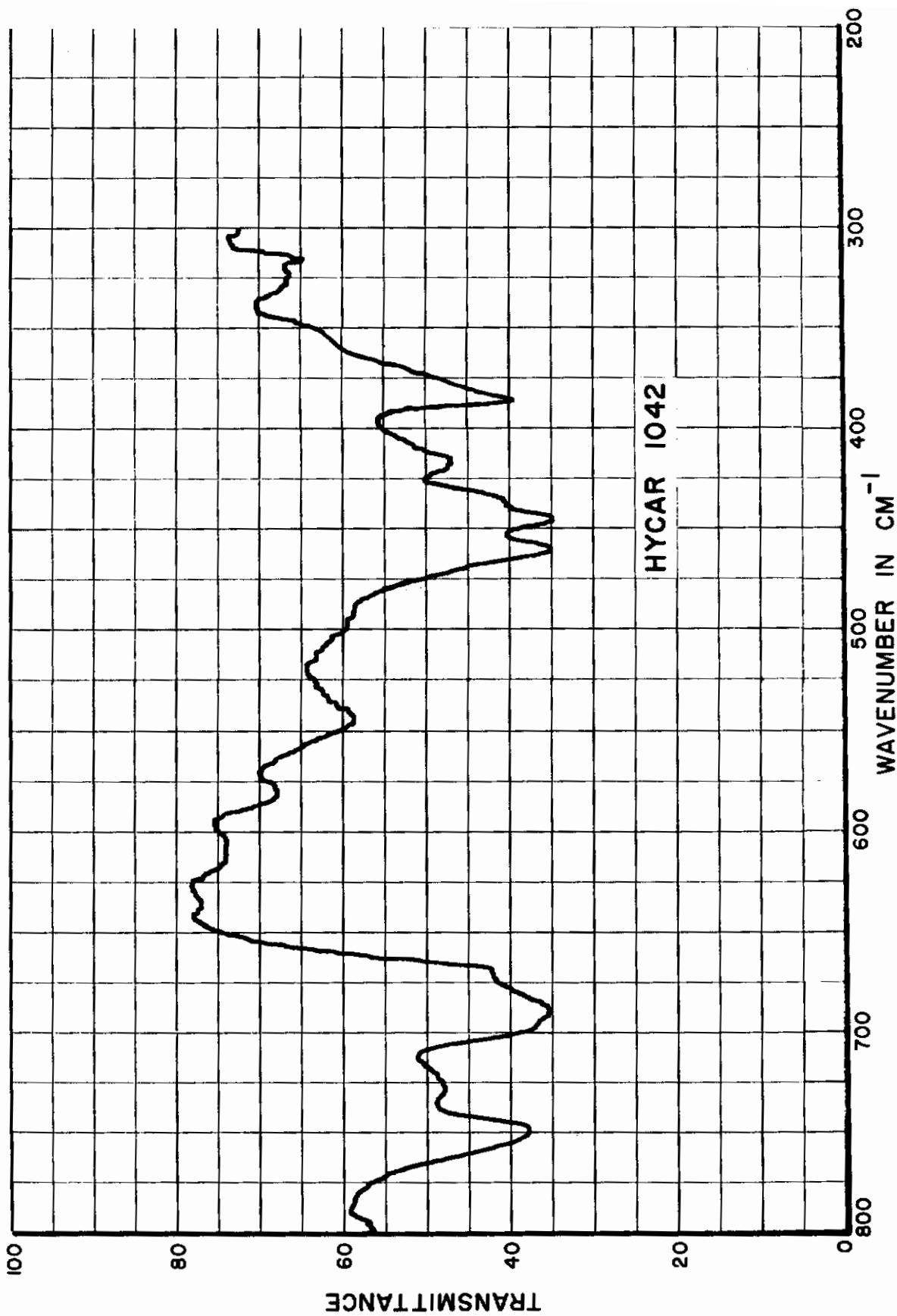


Figure 13. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Hycar 1042 (Butadiene-Acrylonitrile Copolymer; 70:30)  
Recorded as a pressed film approximately 0.16 mm in thickness

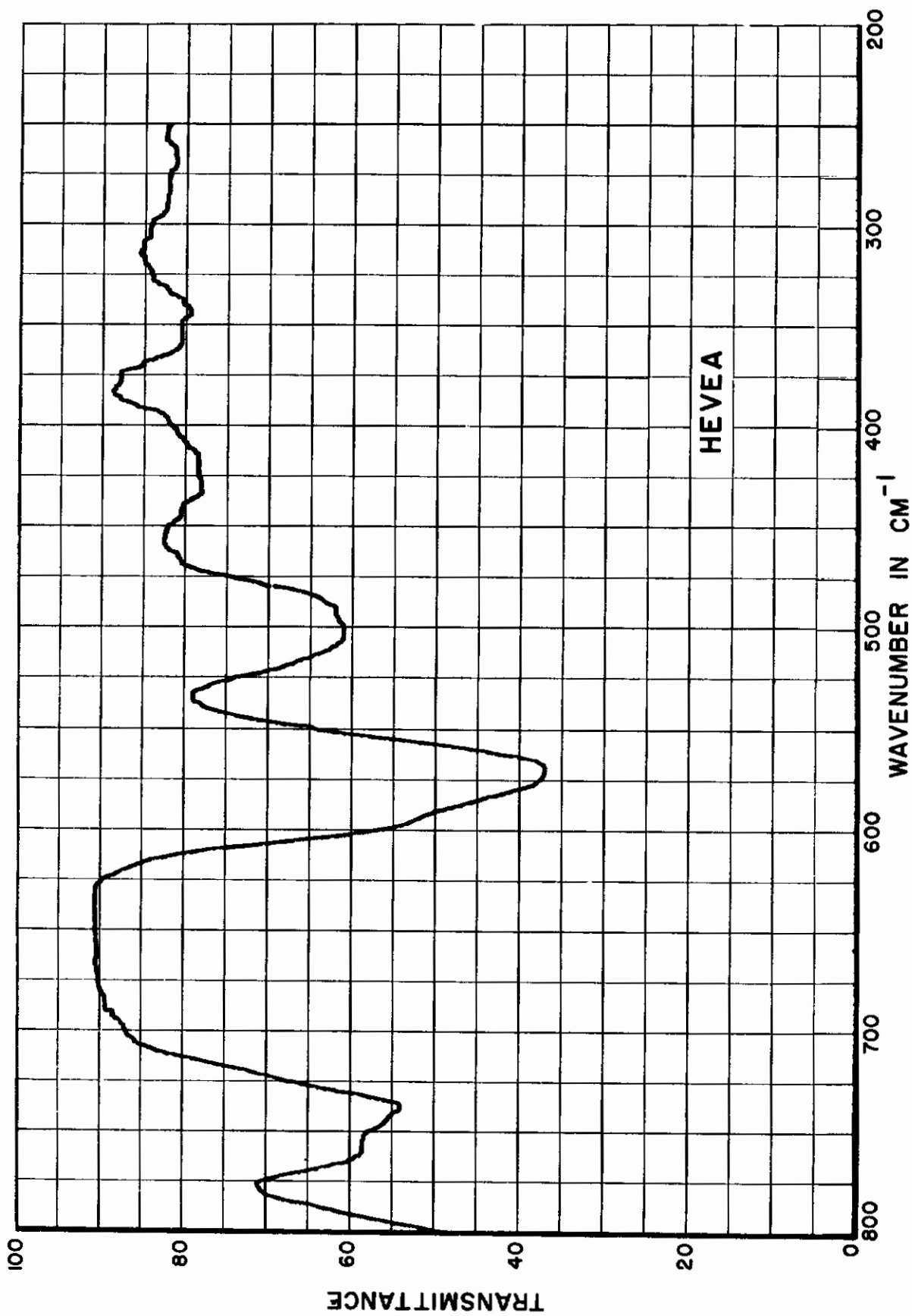


Figure 14. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Hevea (cis 1,4-Polyisoprene)  
Recorded as a film approximately 0.11 mm in thickness,  
prepared from a chloroform solution

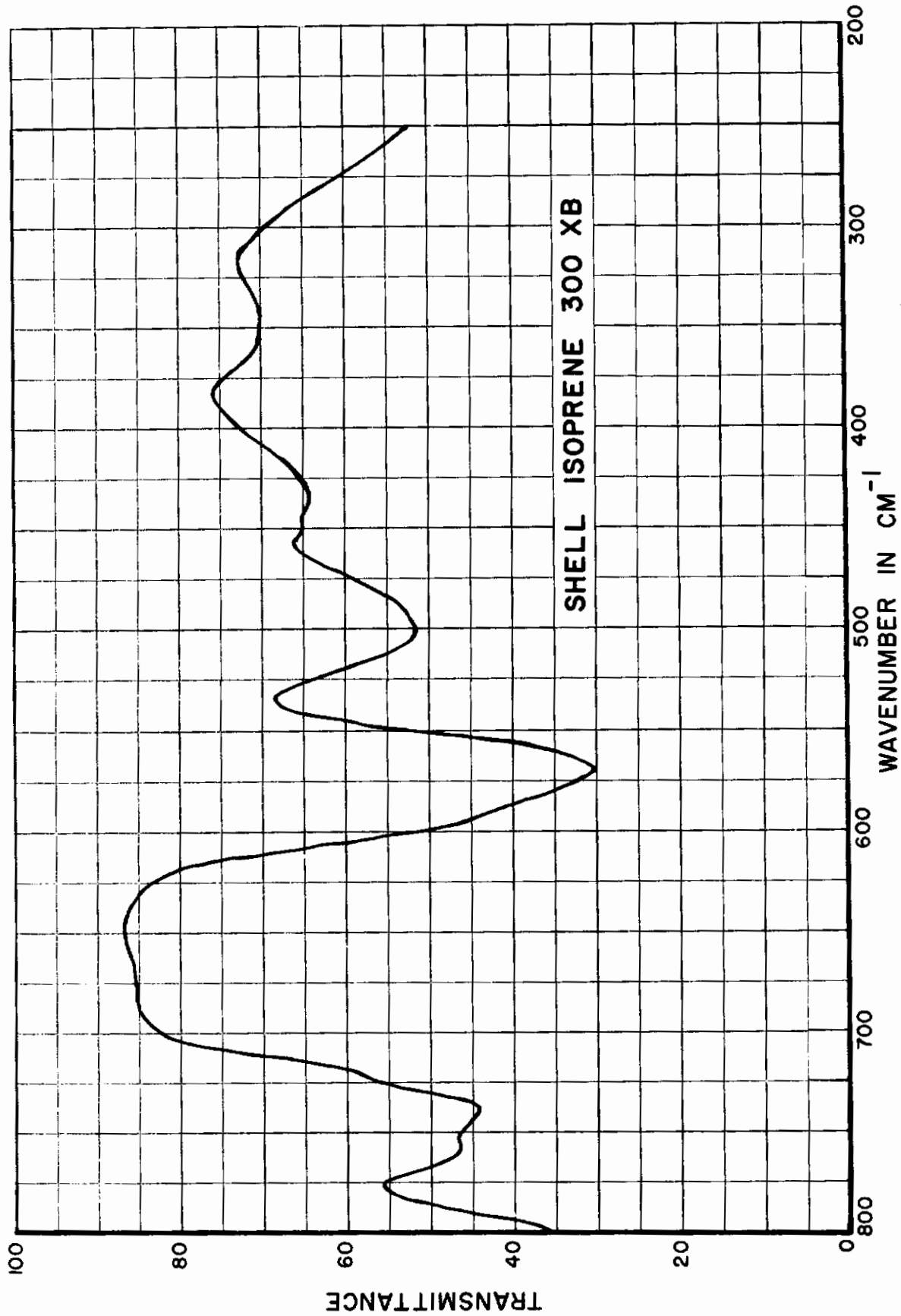


Figure 15. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Shell Isoprene 300 XB (cis 1,4-Polyisoprene)  
Recorded as a film approximately 0.135 mm in thickness, prepared from a  
chloroform solution

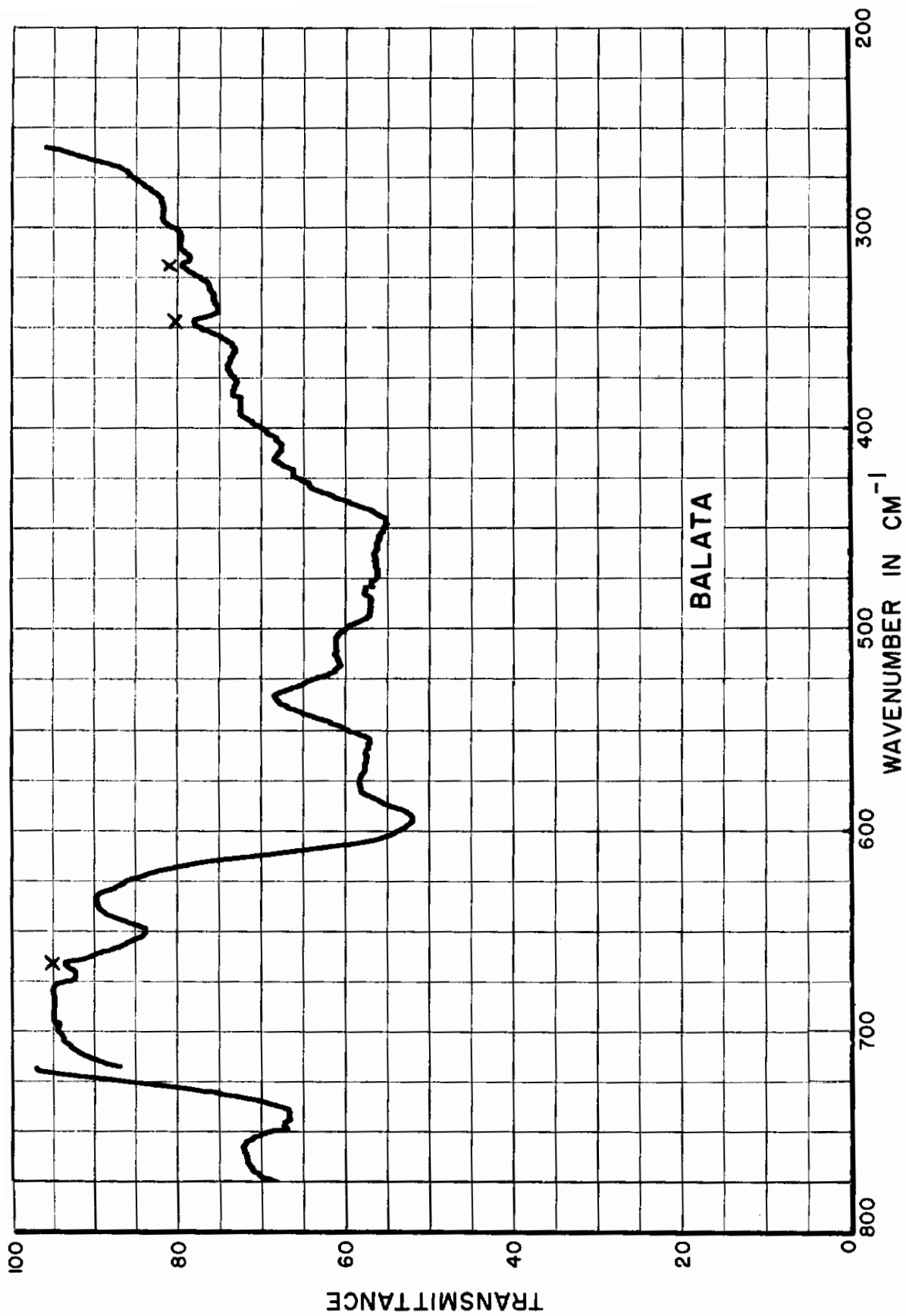


Figure 16. - Infrared Spectrum from 775 - 250 cm<sup>-1</sup> of Balata (trans 1,4-Polyisoprene)  
Recorded as a film prepared from chloroform solution

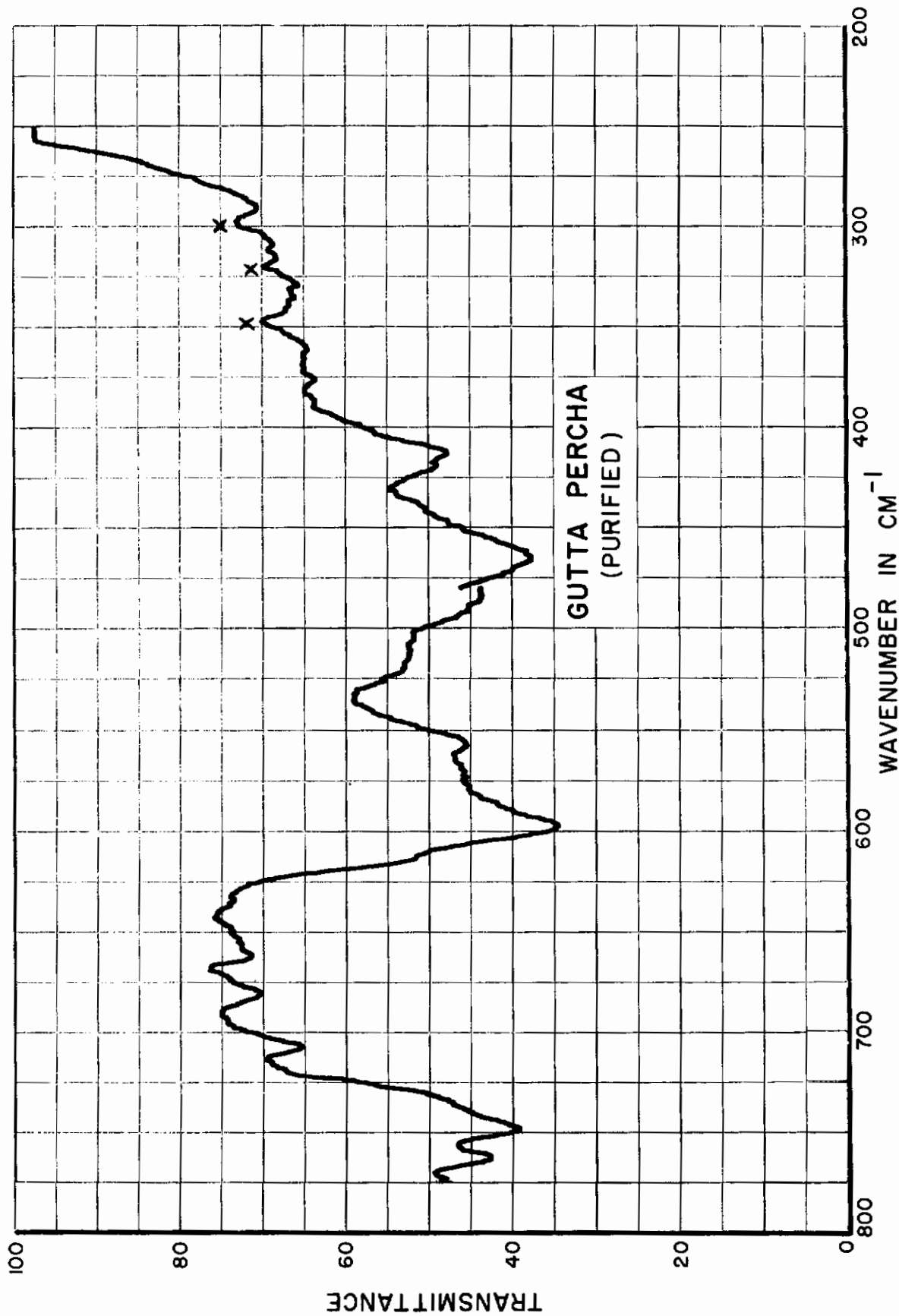


Figure 17. - Infrared Spectrum from 775 - 250 cm<sup>-1</sup> of Gutta Percha (Crystalline trans 1,4-Polyisoprene)  
Recorded as a film prepared from chloroform solution

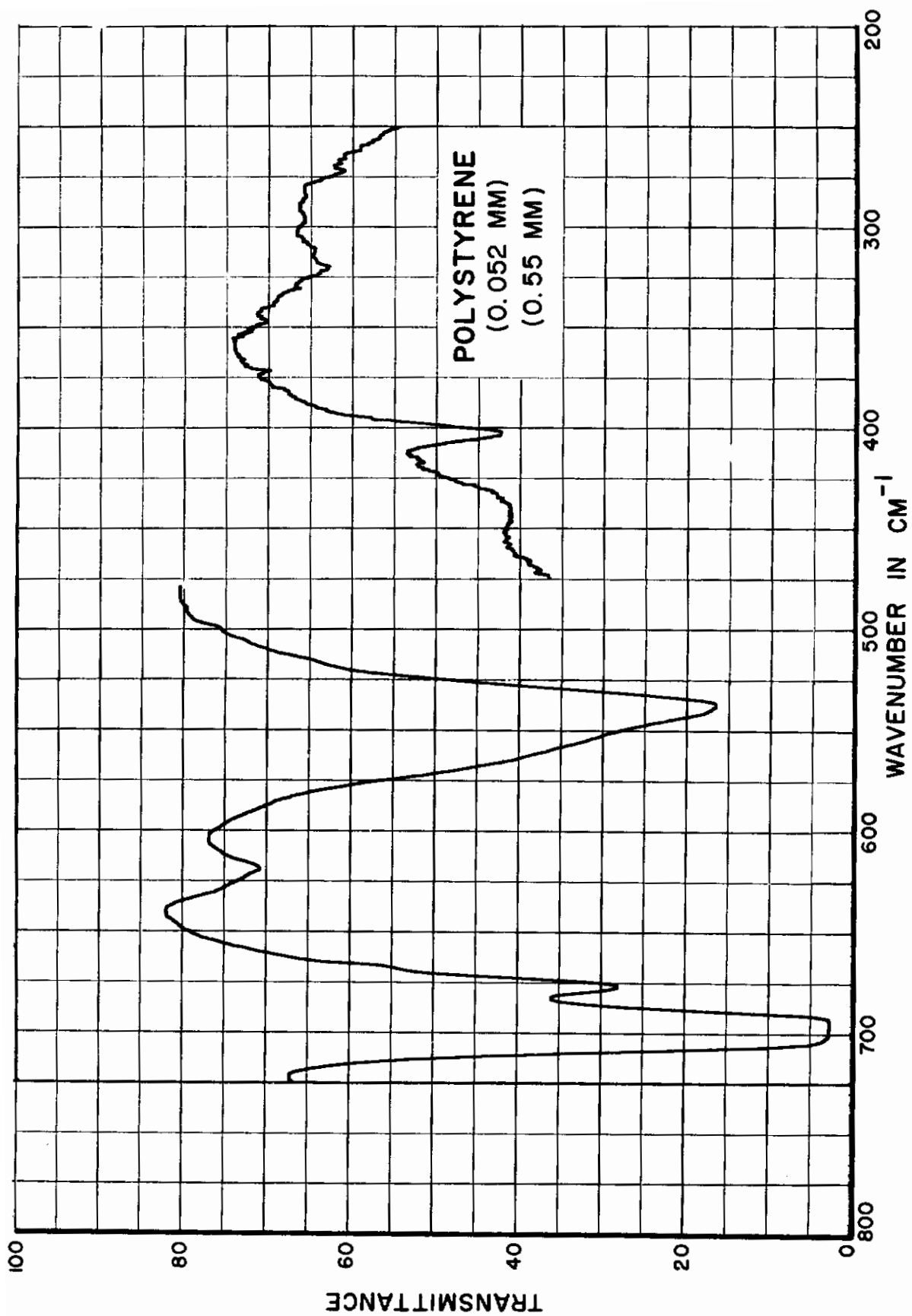


Figure 18. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Polystyrene (Atactic, Amorphous)  
Recorded as a film

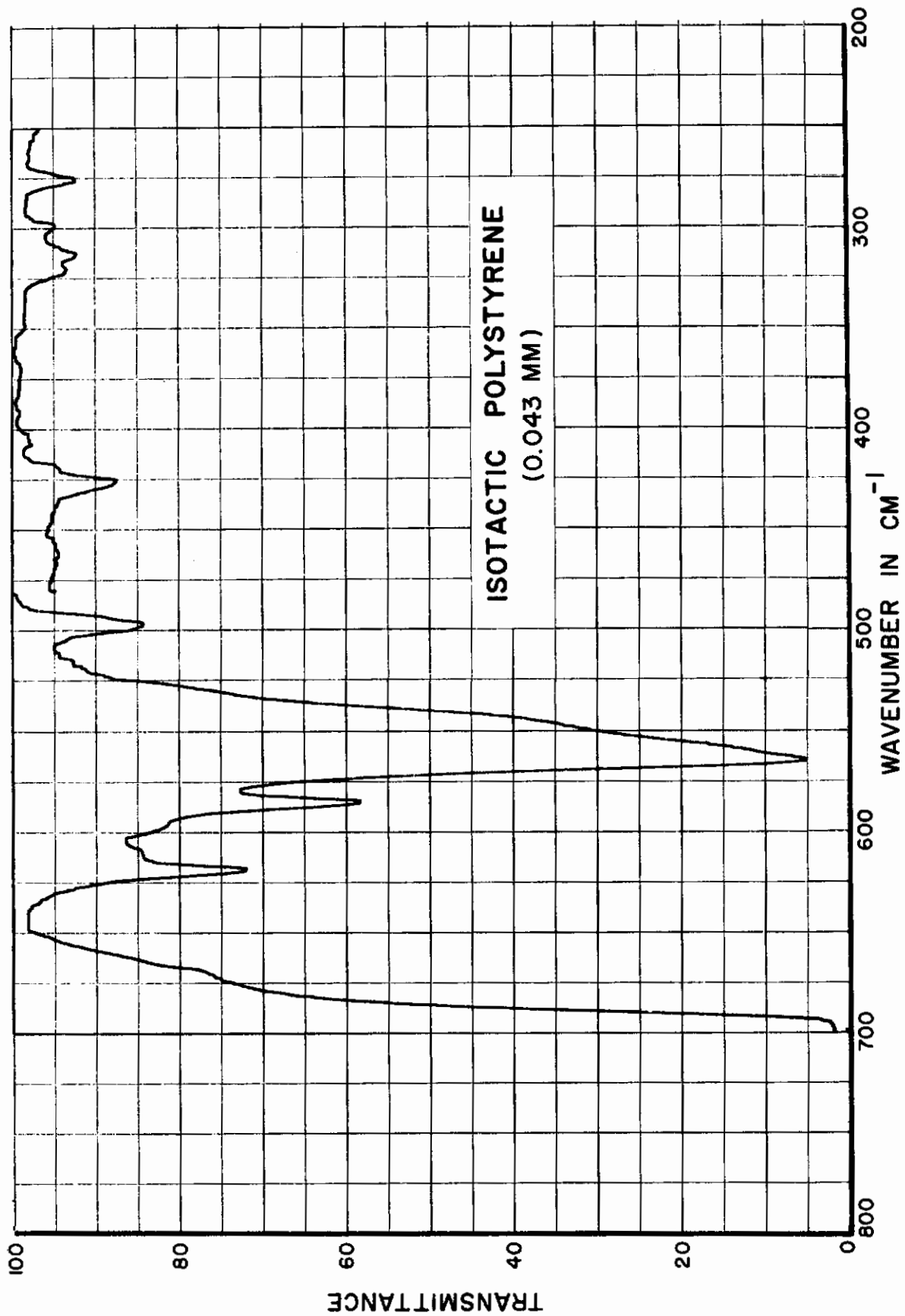


Figure 19. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Polystyrene (Isotactic, Crystalline)  
Recorded as a film, prepared from benzene solution



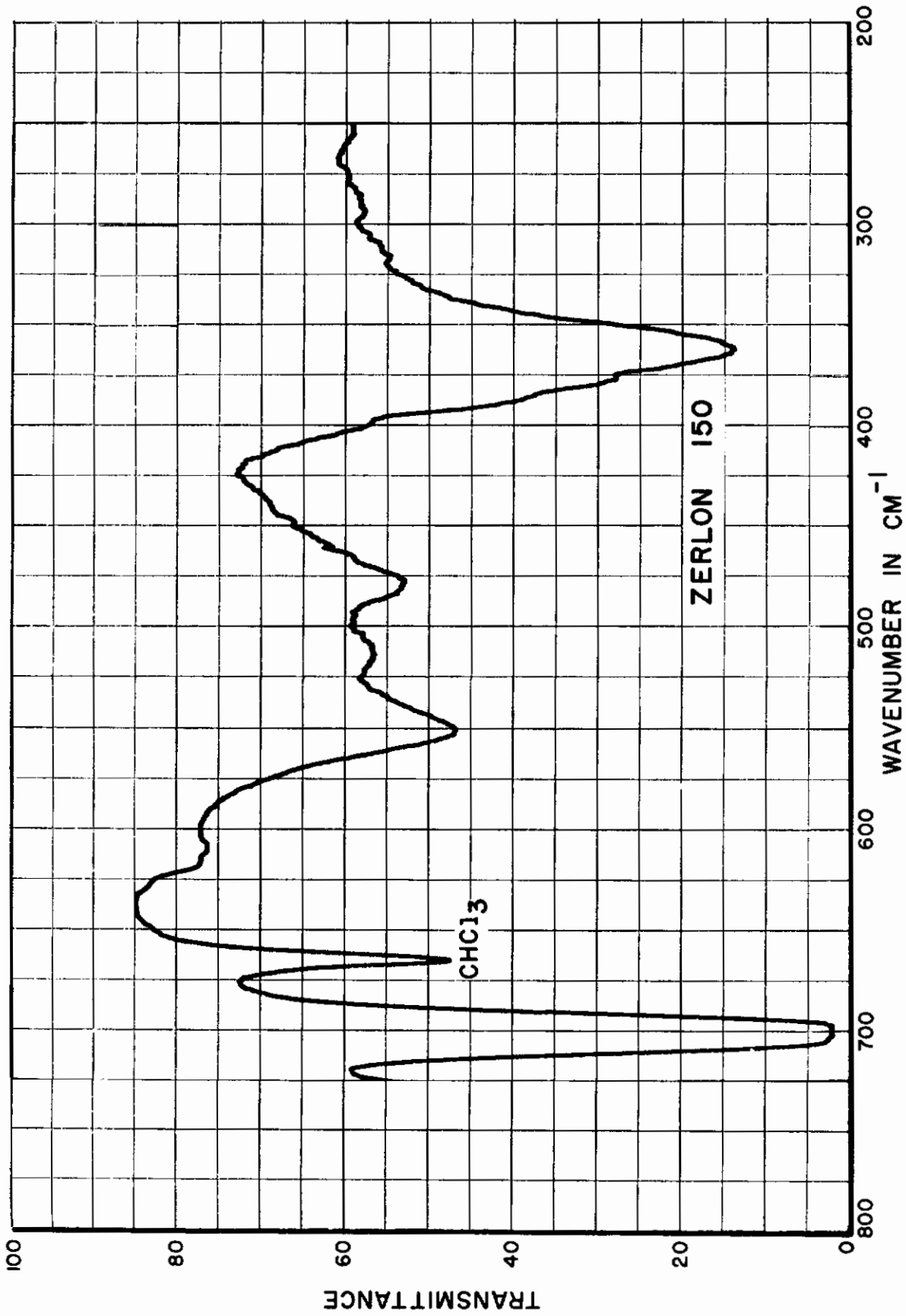


Figure 20. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Zerlon 50 (Styrene-Methyl Methacrylate Copolymer 50:50)  
Recorded as a film approximately 0.085 mm in thickness, prepared from a chloroform solution

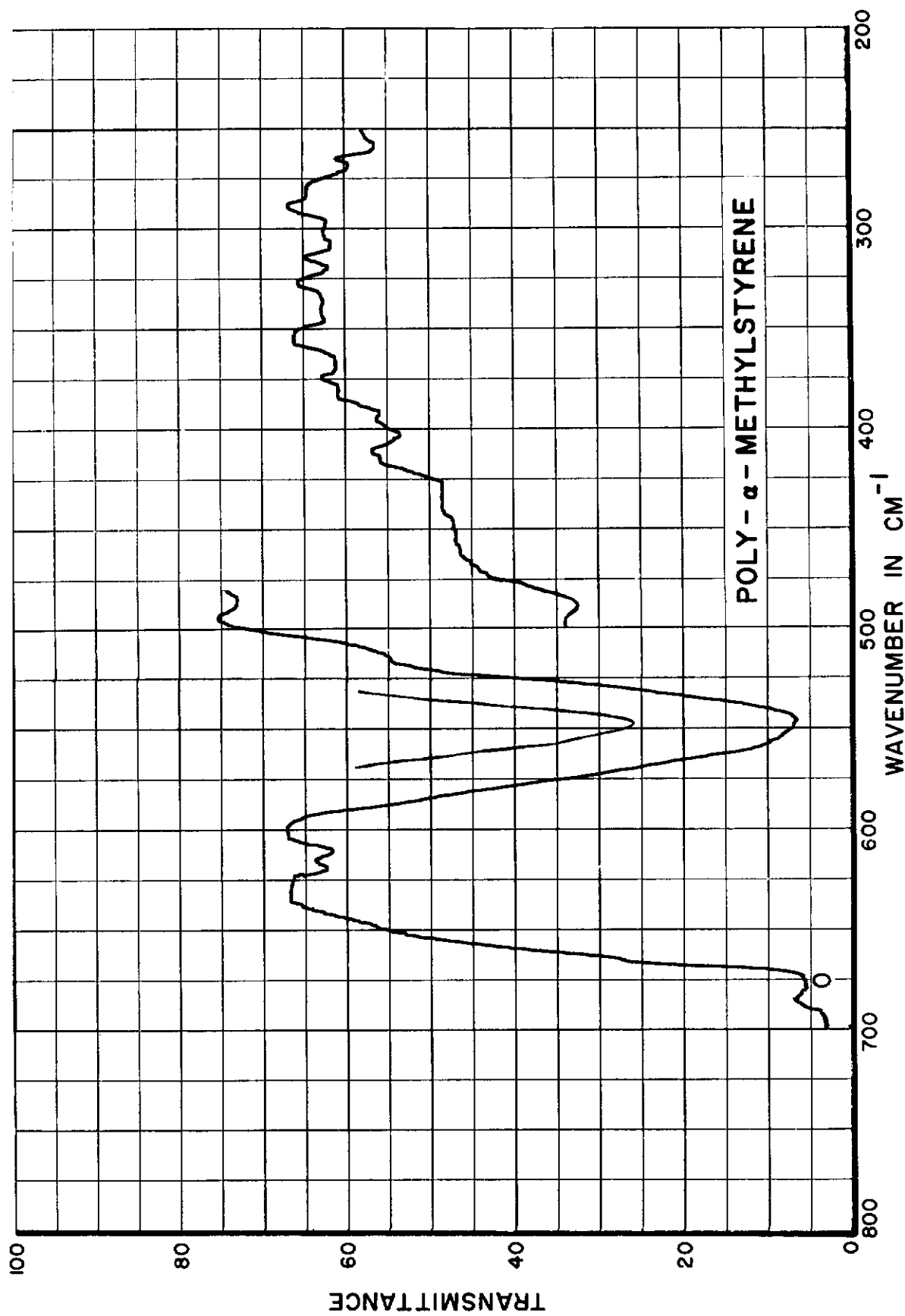


Figure 21. - Infrared Spectrum from 700 - 250  $\text{cm}^{-1}$  of Poly- $\alpha$ -Methylstyrene  
Recorded as a film, prepared from a chloroform solution

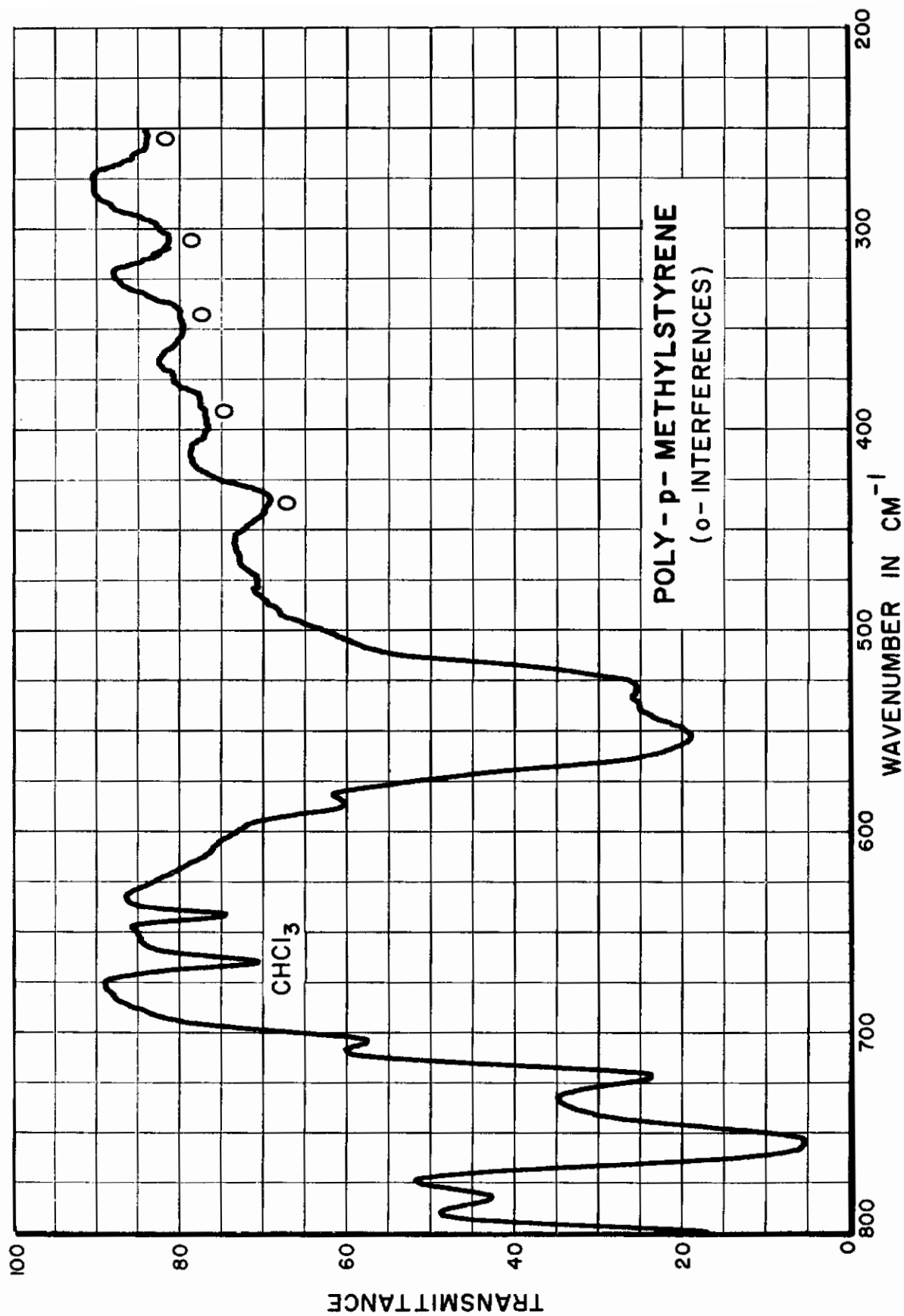


Figure 22. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Poly-p-Methylstyrene (Atactic)  
Recorded as a film approximately 0.025 mm in thickness,  
prepared from chloroform solution

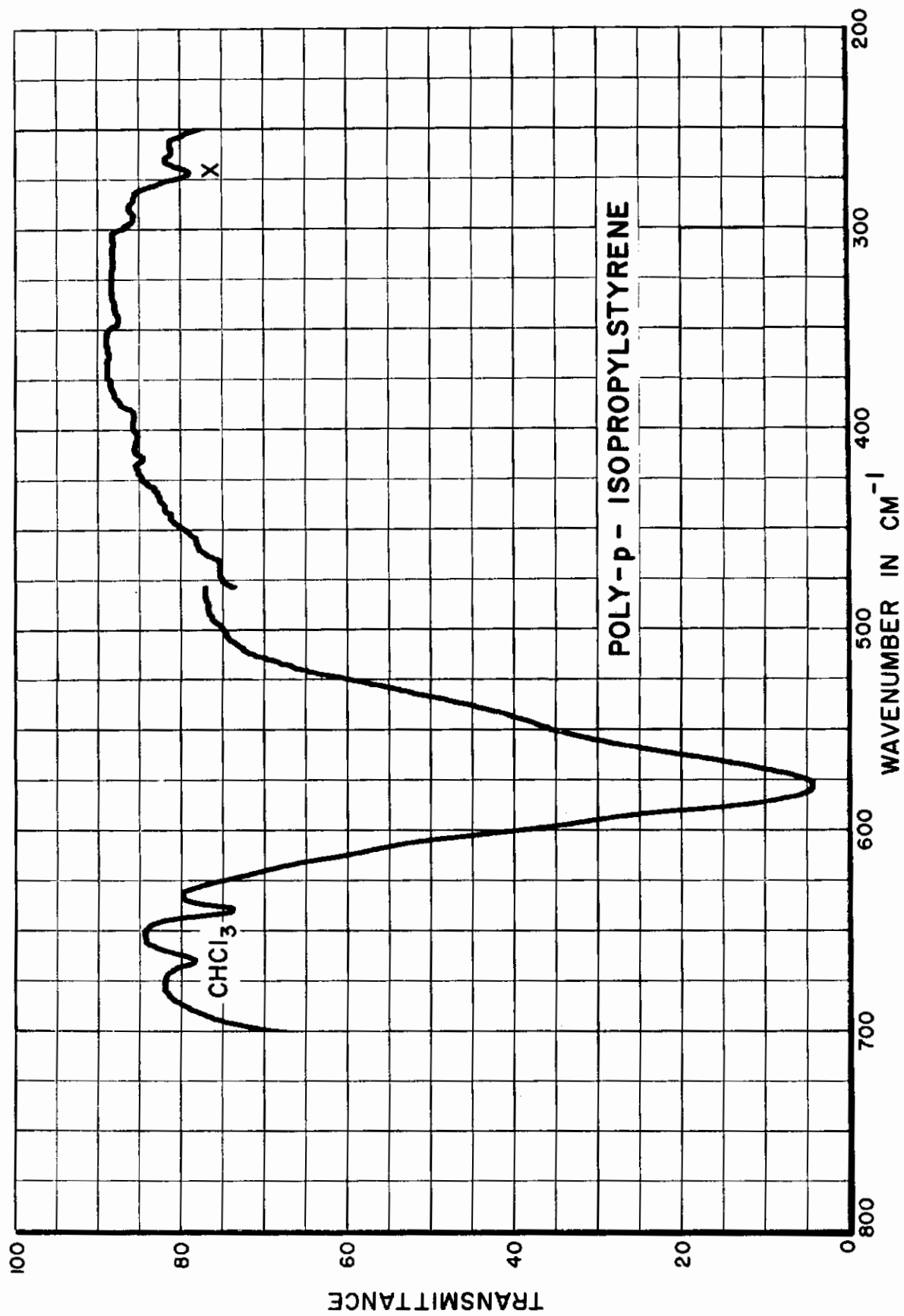


Figure 23. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Poly-p-Isopropylstyrene (Atactic)  
Recorded as a film approximately 0.05 mm in thickness, prepared  
from a chloroform solution

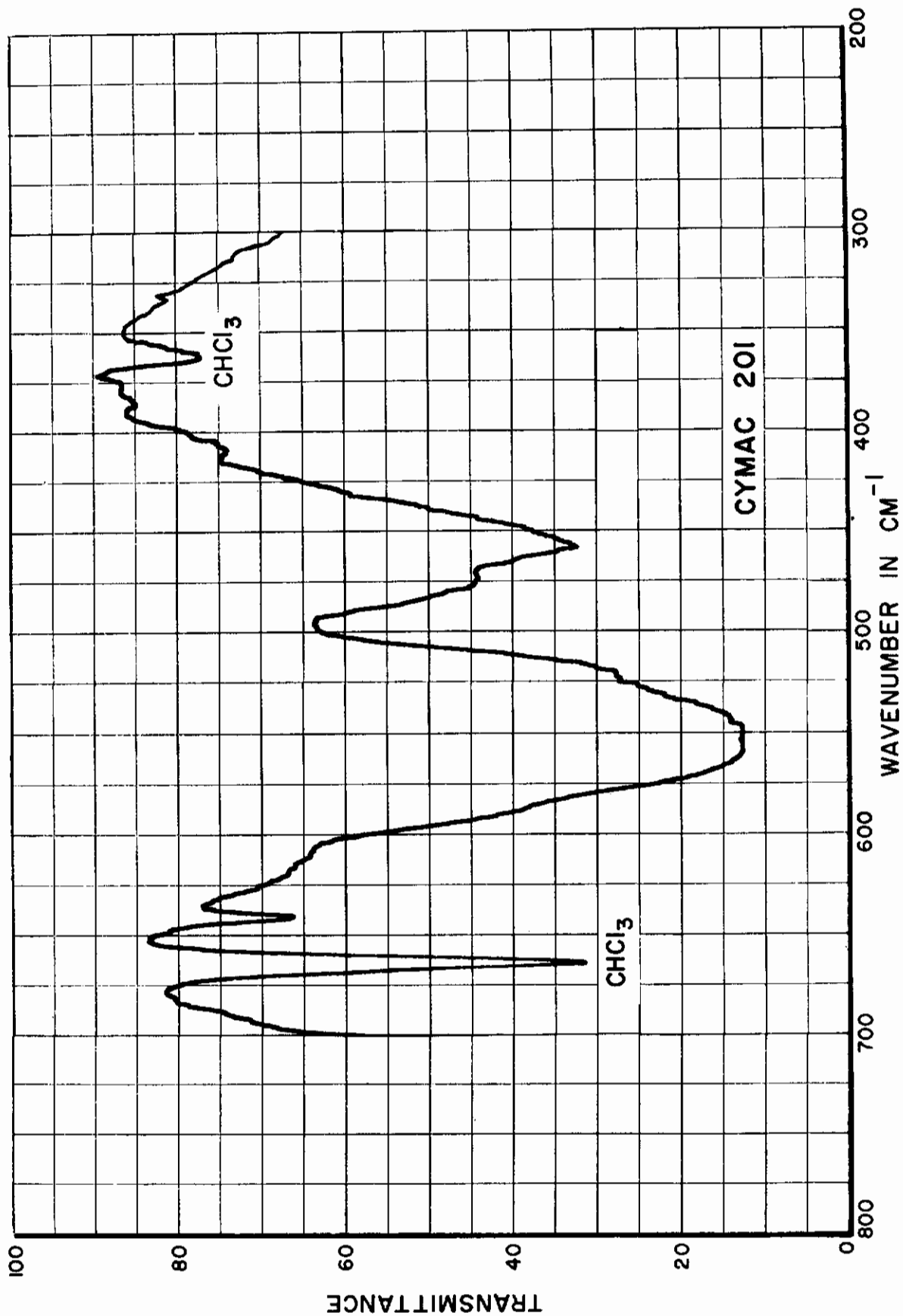


Figure 24. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Cymac 201 (Vinyltoluene-Acrylonitrile Copolymer 70:30)

Recorded as a film approximately 0.15 mm in thickness, prepared from a chloroform solution

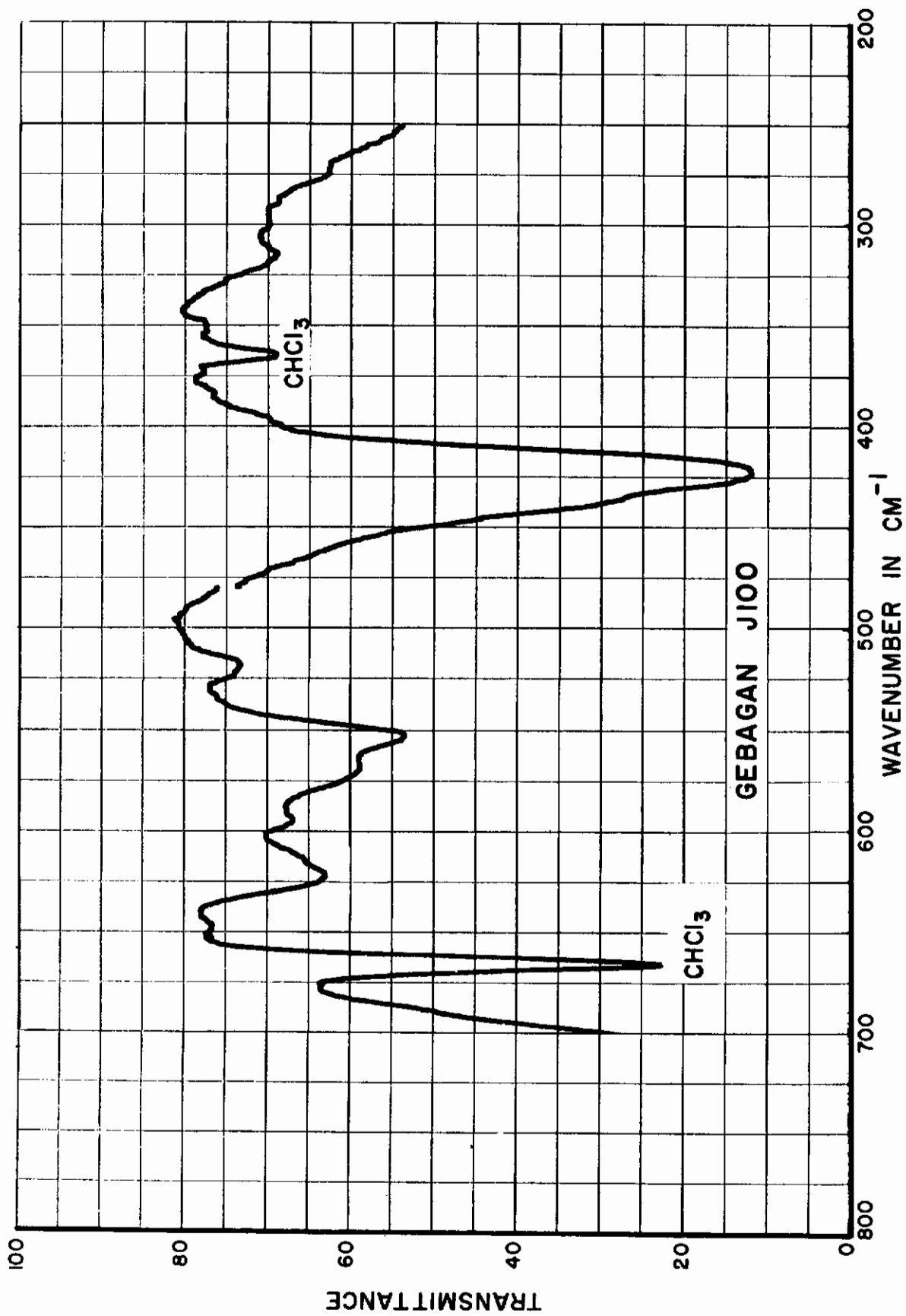


Figure 25. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Gebagan J100 (Polyindene)  
Recorded as a film, prepared from a chloroform solution

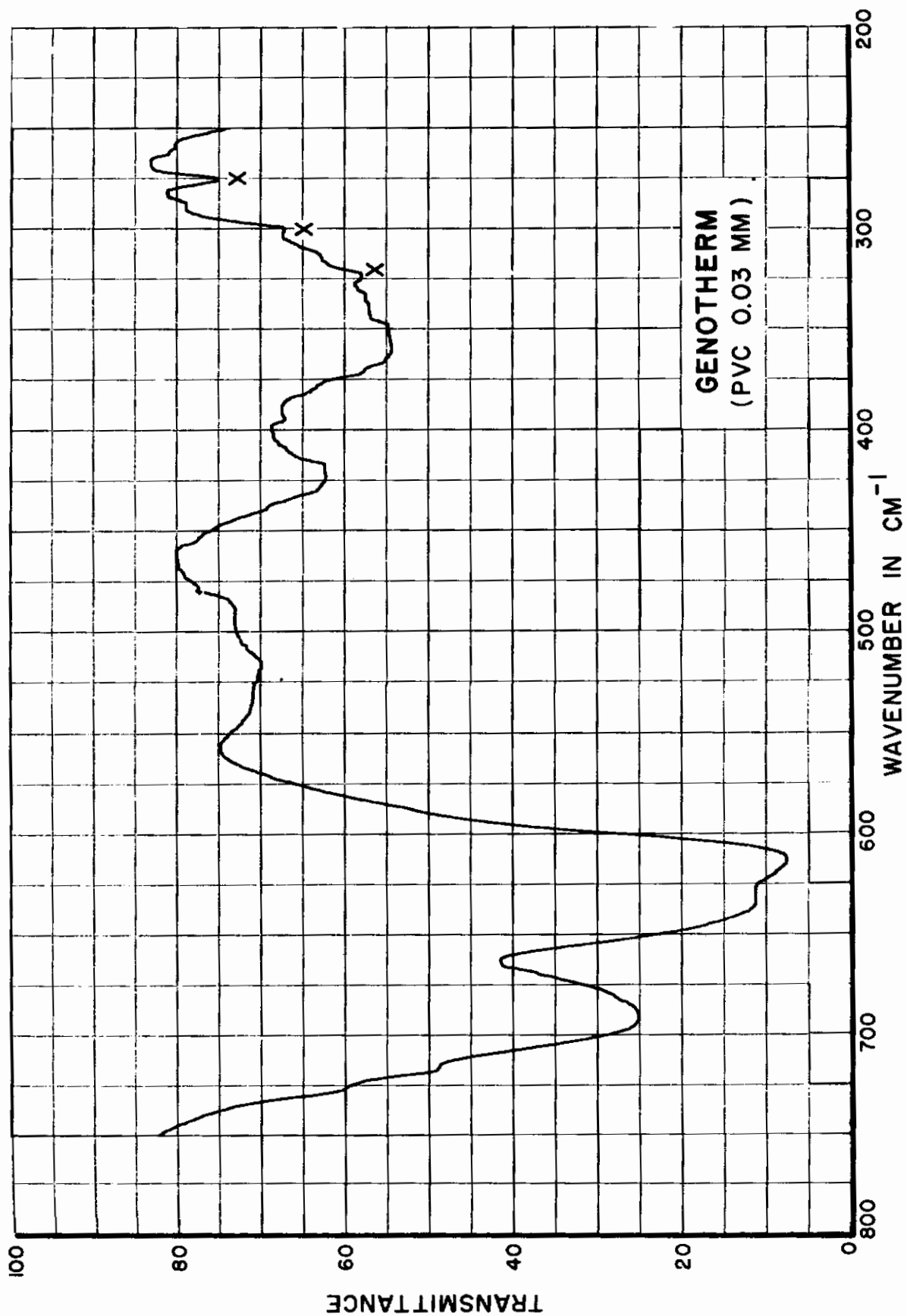


Figure 26. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Genotherm Kalle (Polyvinylchloride)  
Recorded as a film approximately 0.03 mm in thickness

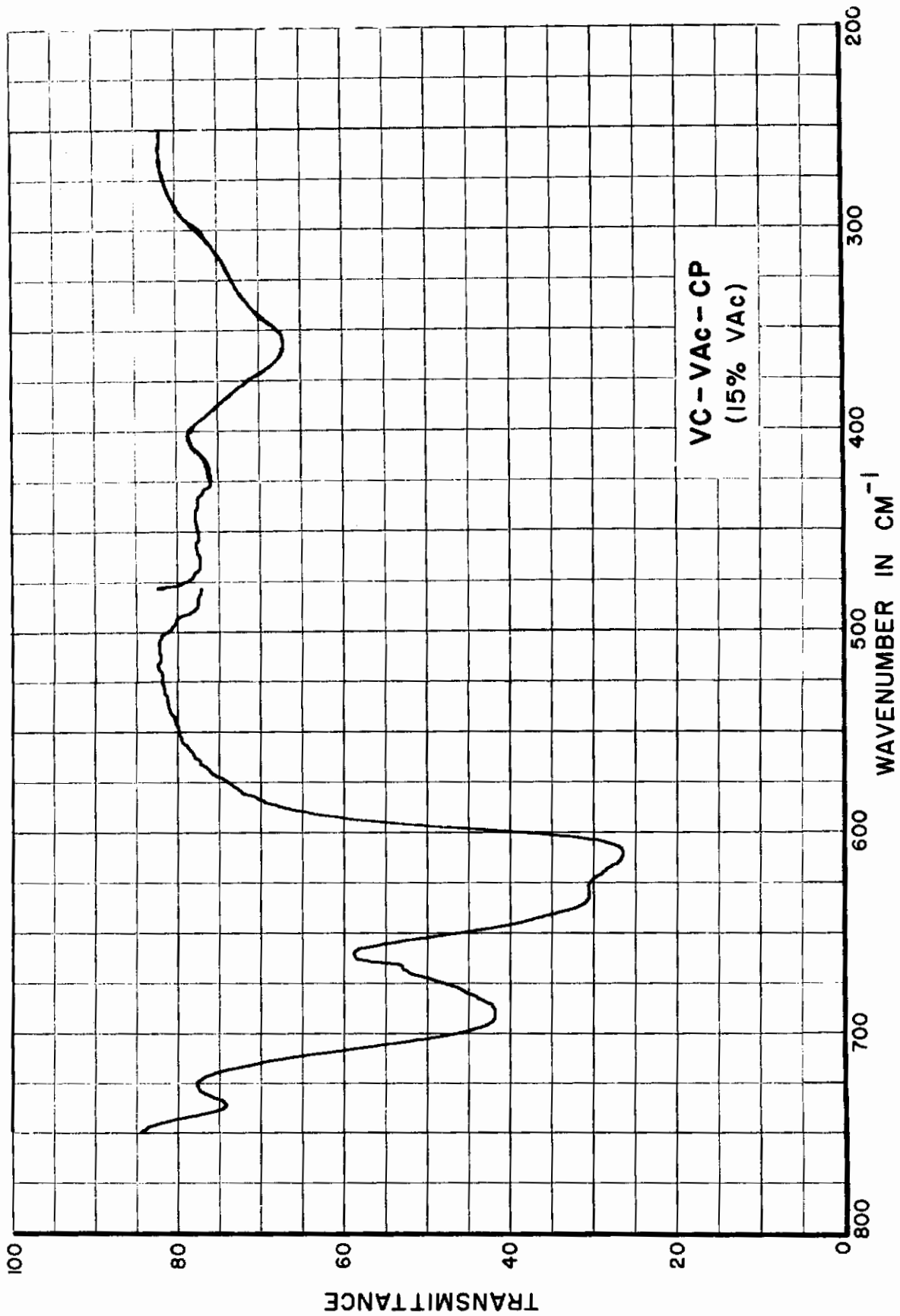


Figure 27. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of VC-VAc-CP (Vinyl Chloride-Vinyl Acetate Copolymer 85:15)  
Recorded as a film approximately 0.03 mm in thickness



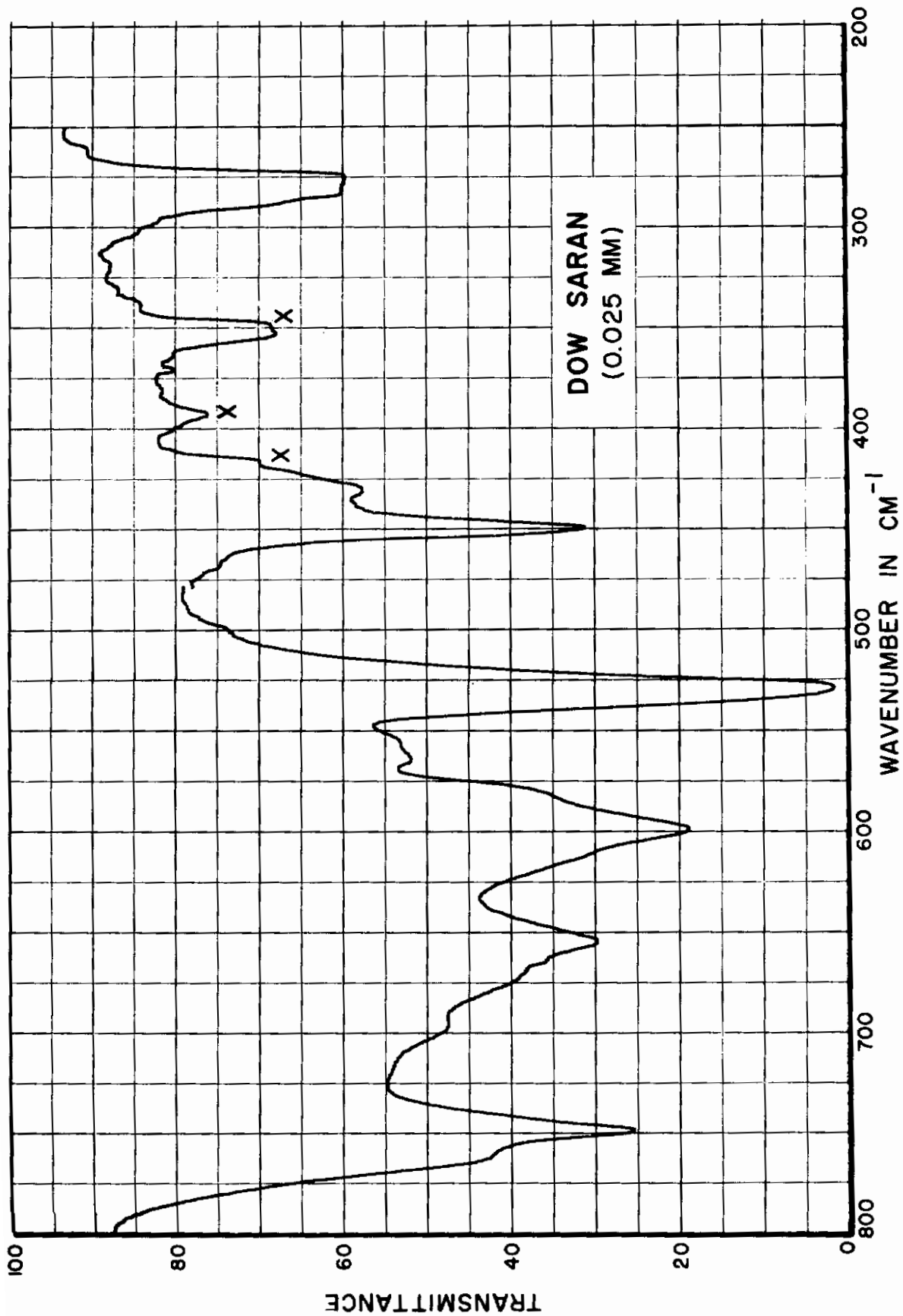


Figure 28. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Dow Saran (Polyvinylidene Chloride with an Ester Type Copolymer)  
Recorded as a film 0.025 mm in thickness

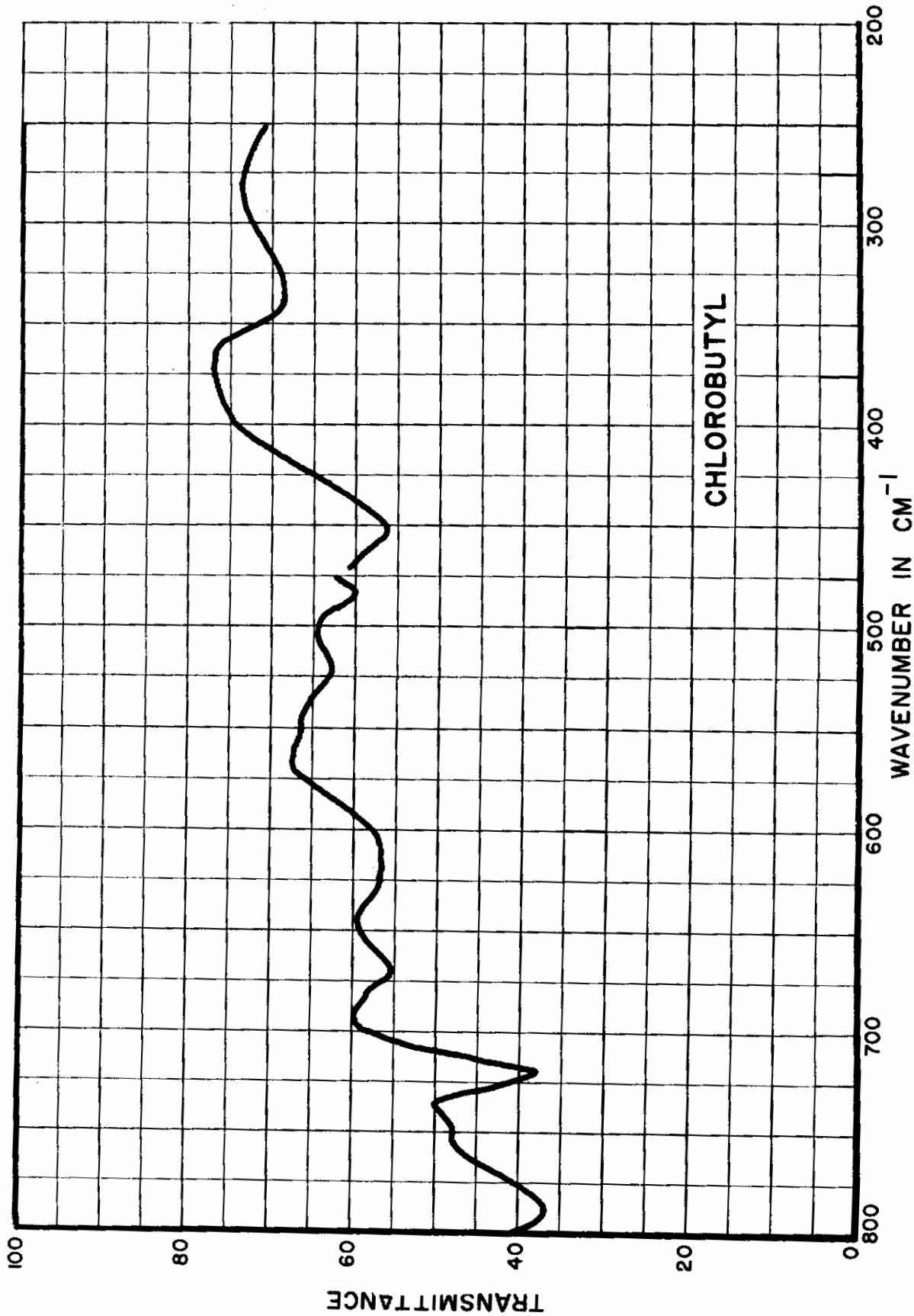
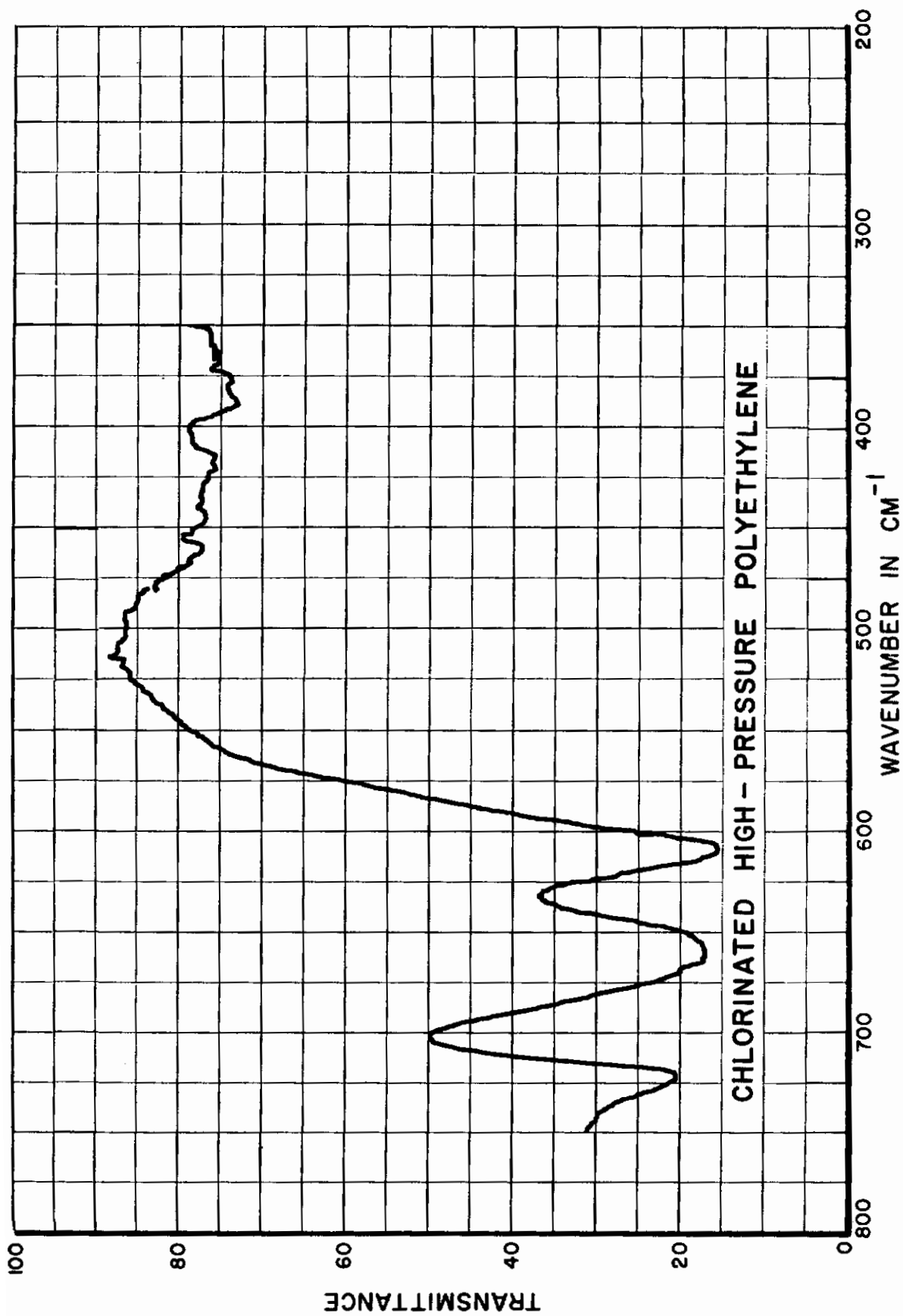


Figure 29. - Infrared Spectrum from 800 - 250  $\text{cm}^{-1}$  of Chlorobutyl (Low Chlorinated Polyisobutylene)  
Recorded as a pressed film



CHLORINATED HIGH - PRESSURE POLYETHYLENE

Figure 30. - Infrared Spectrum from 750 - 350 cm<sup>-1</sup> of Chlorinated High Pressure Polyethylene  
Recorded as a pressed film approximately 0.1 mm in thickness

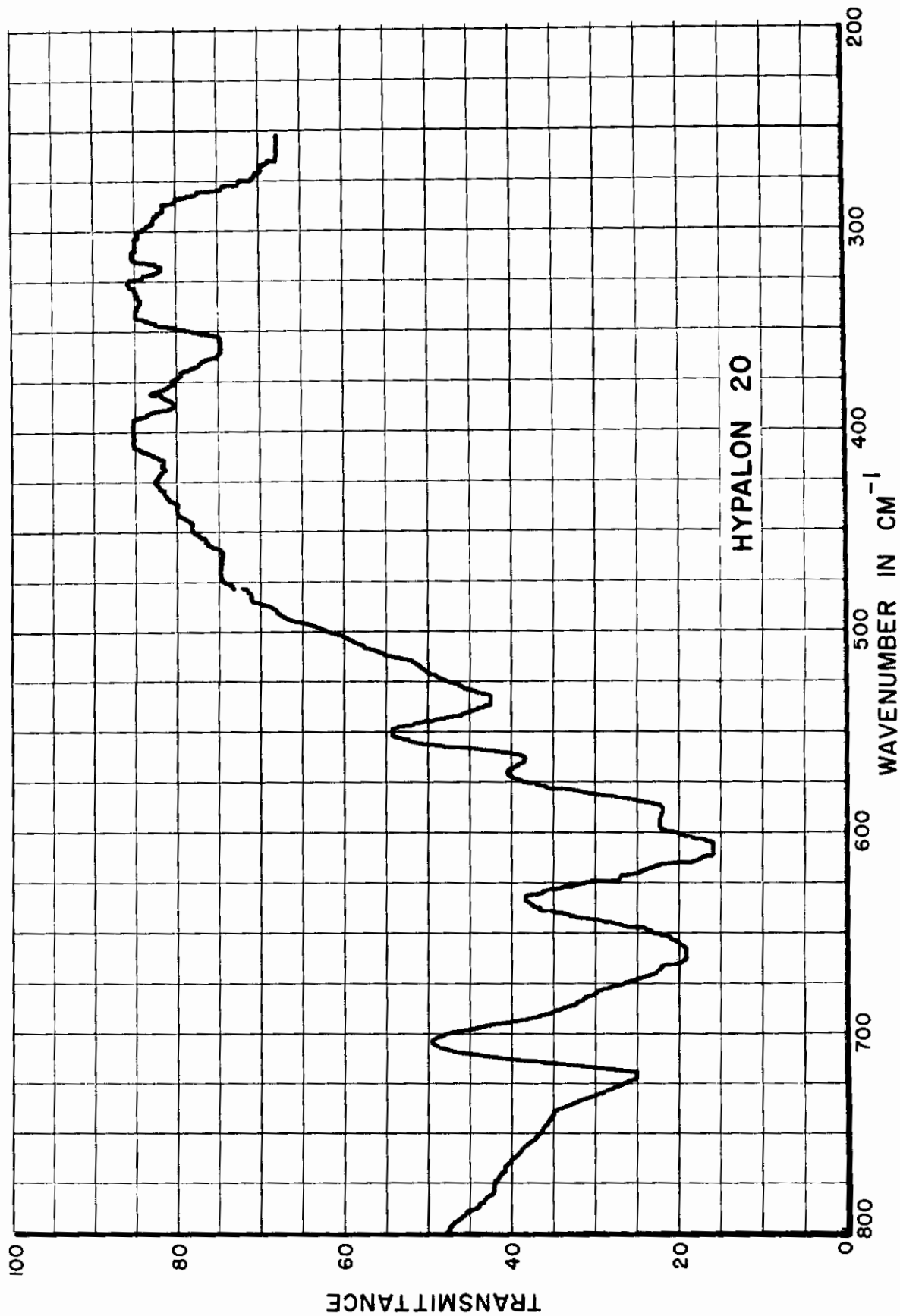


Figure 31. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Hypalon 20 (Sulfochlorinated High Pressure Polyethylene)  
Recorded as a pressed film

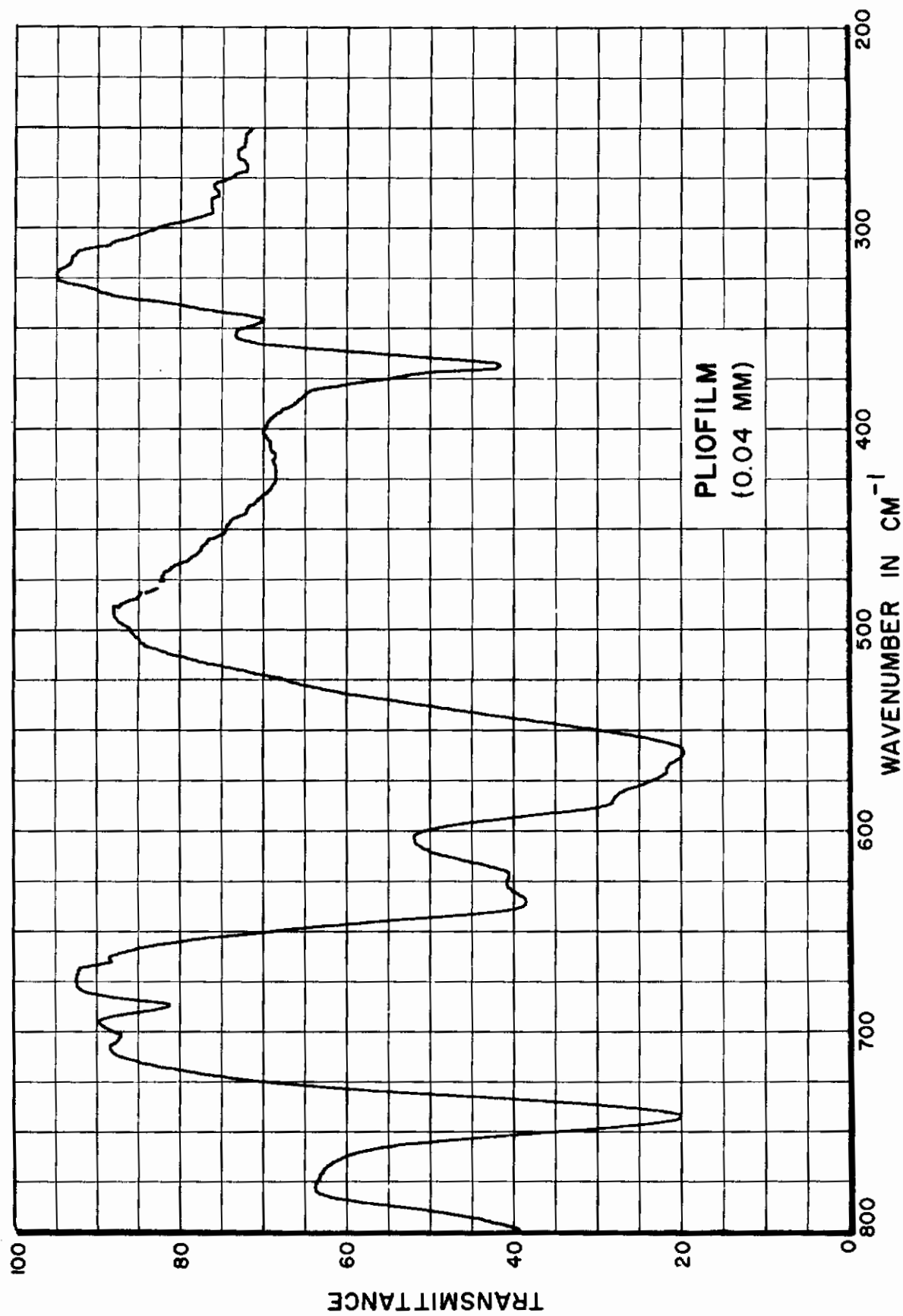


Figure 32. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Pliofilm Kalle (Rubber Hydrochloride)  
Recorded as a film 0.04 mm in thickness

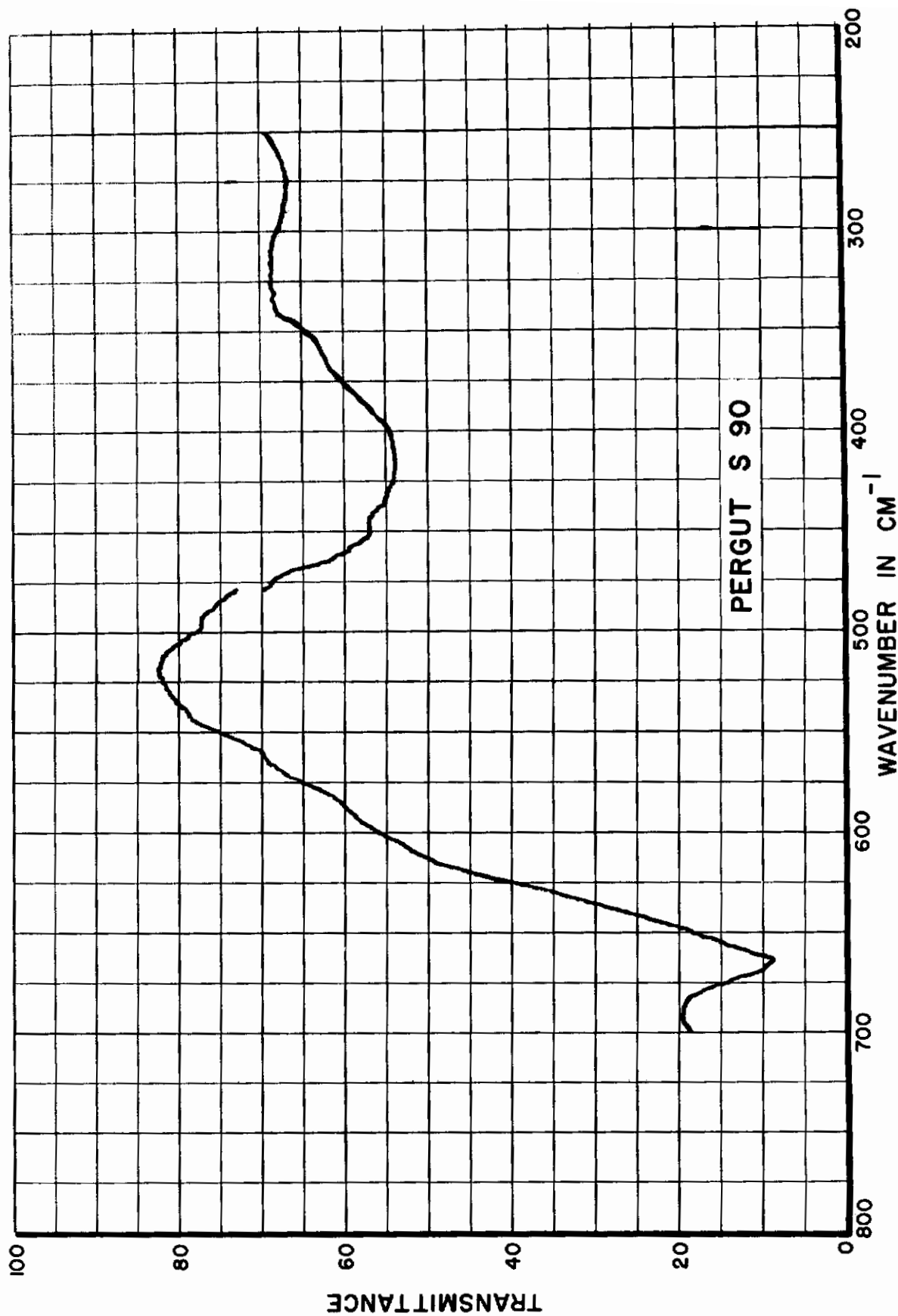


Figure 33. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Pergut S 90 (Chlorinated Rubber)  
Recorded as a film approximately 0.05 mm in thickness, prepared  
from a chloroform solution

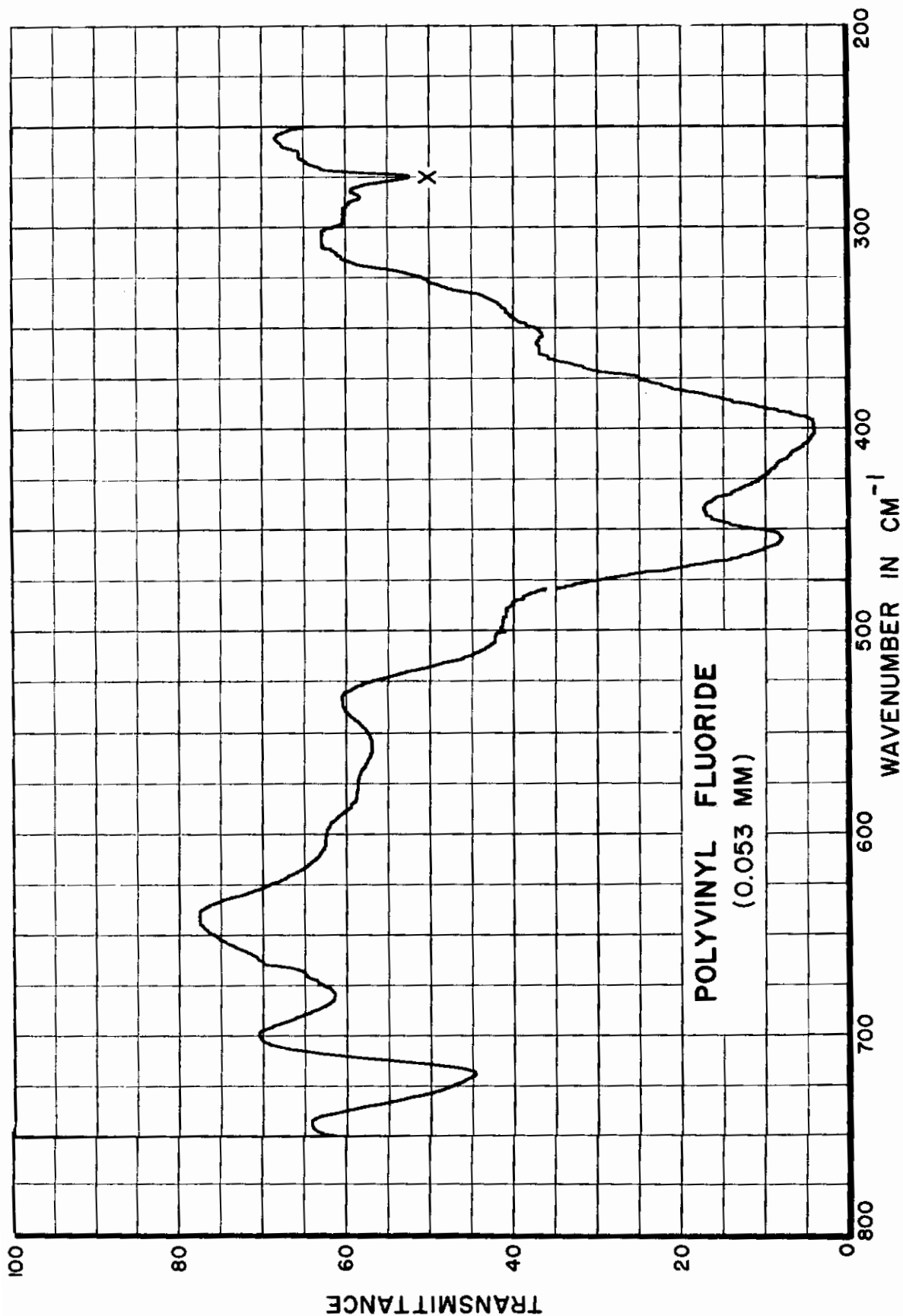


Figure 34. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Teslar (Polyvinylfluoride) Recorded as a film 0.053 mm in thickness

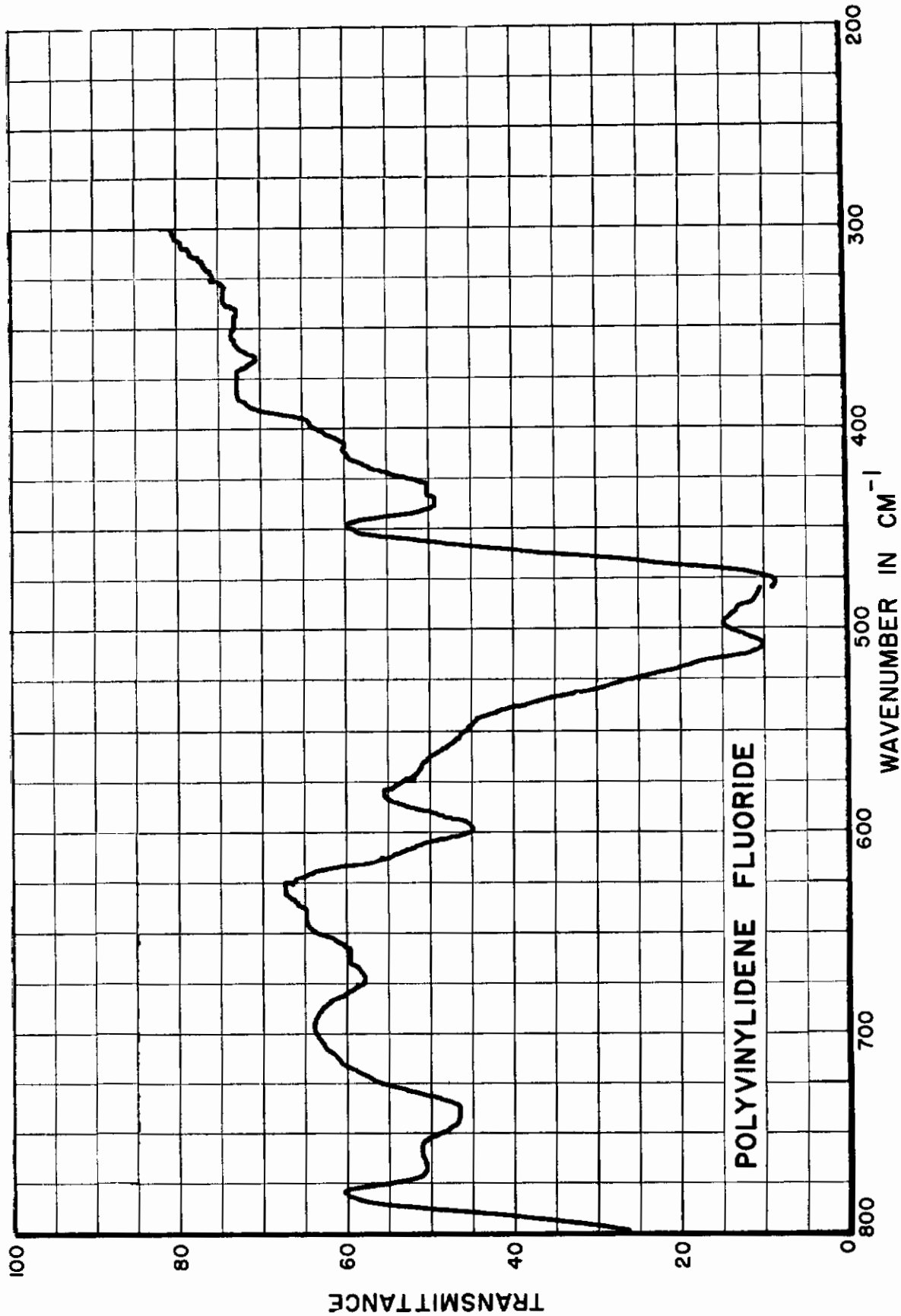


Figure 35. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Polyvinylidene Fluoride  
Recorded as a film approximately 0.05 mm in thickness  
prepared from dimethyl formamide solution



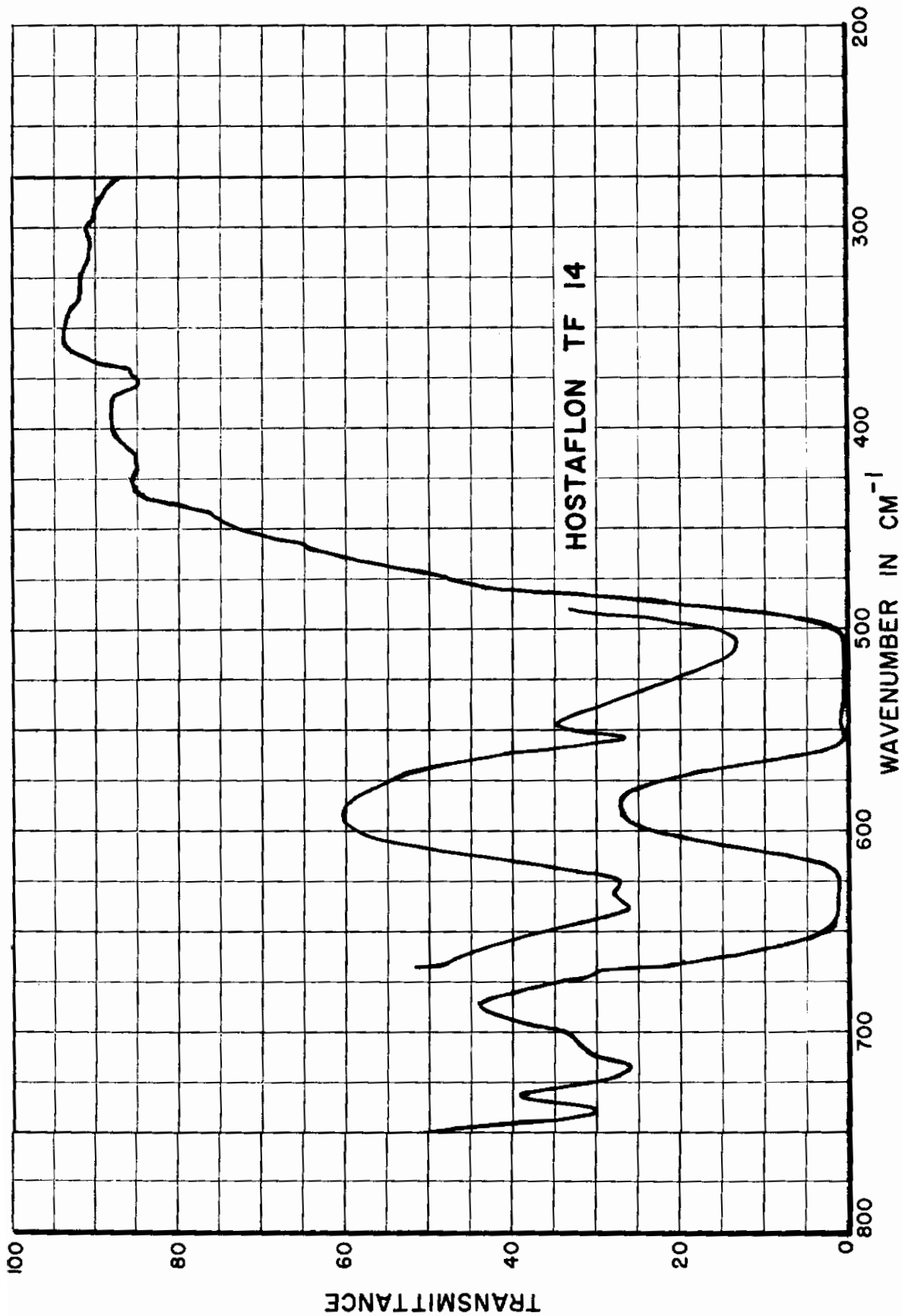
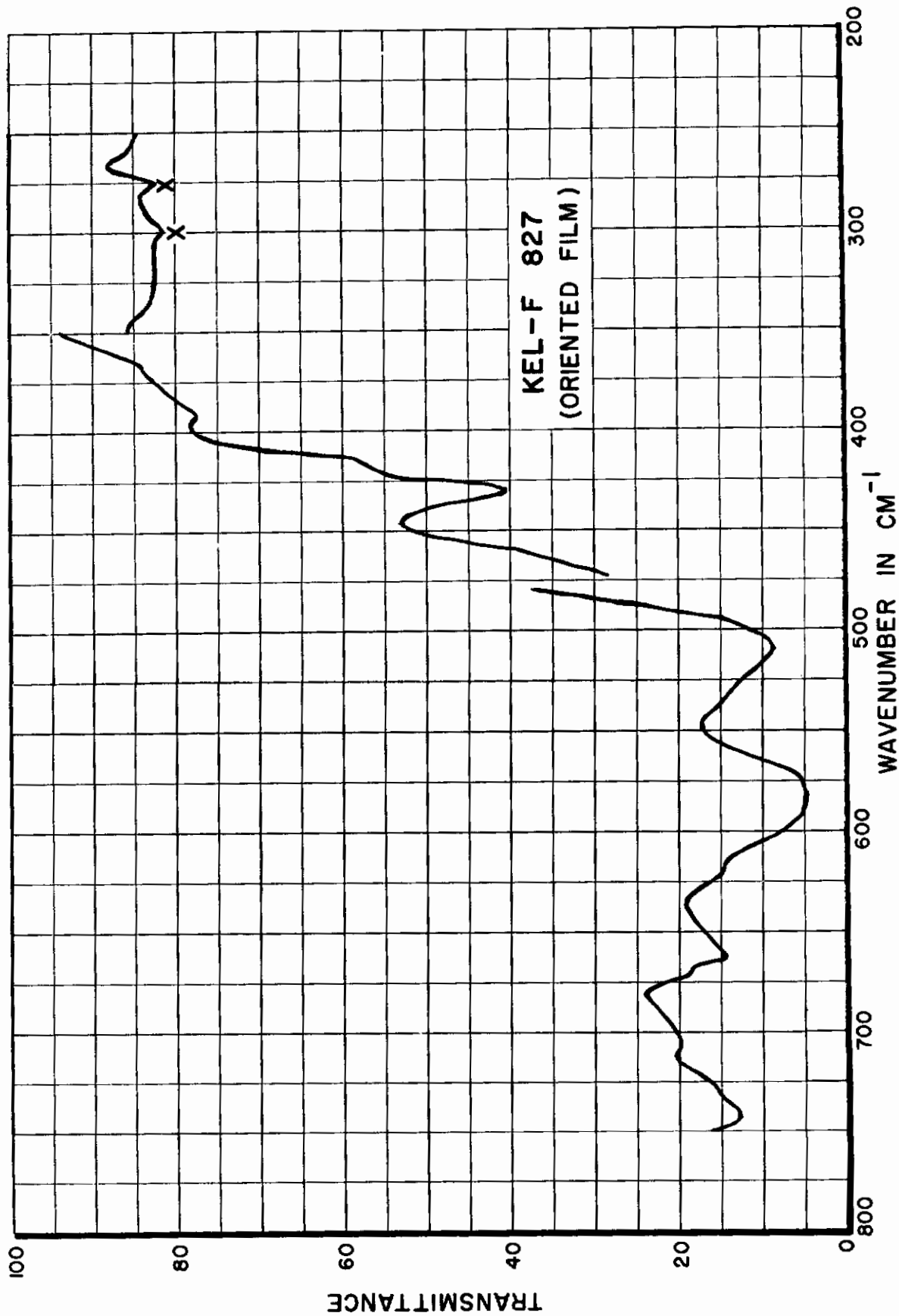


Figure 36. - Infrared Spectrum from 750 - 275 cm<sup>-1</sup> of Hostaflon TF 14 (Polytetrafluoroethylene) Recorded as 0.02 mm KBr disc (upper curve) and thin slices (lower curve)



KEL-F 827  
(ORIENTED FILM)

Figure 37. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Kel-F 827 (Chlorotrifluoroethylene-Vinylidene Fluoride Copolymer)  
Recorded as oriented film approximately 0.04 mm in thickness.

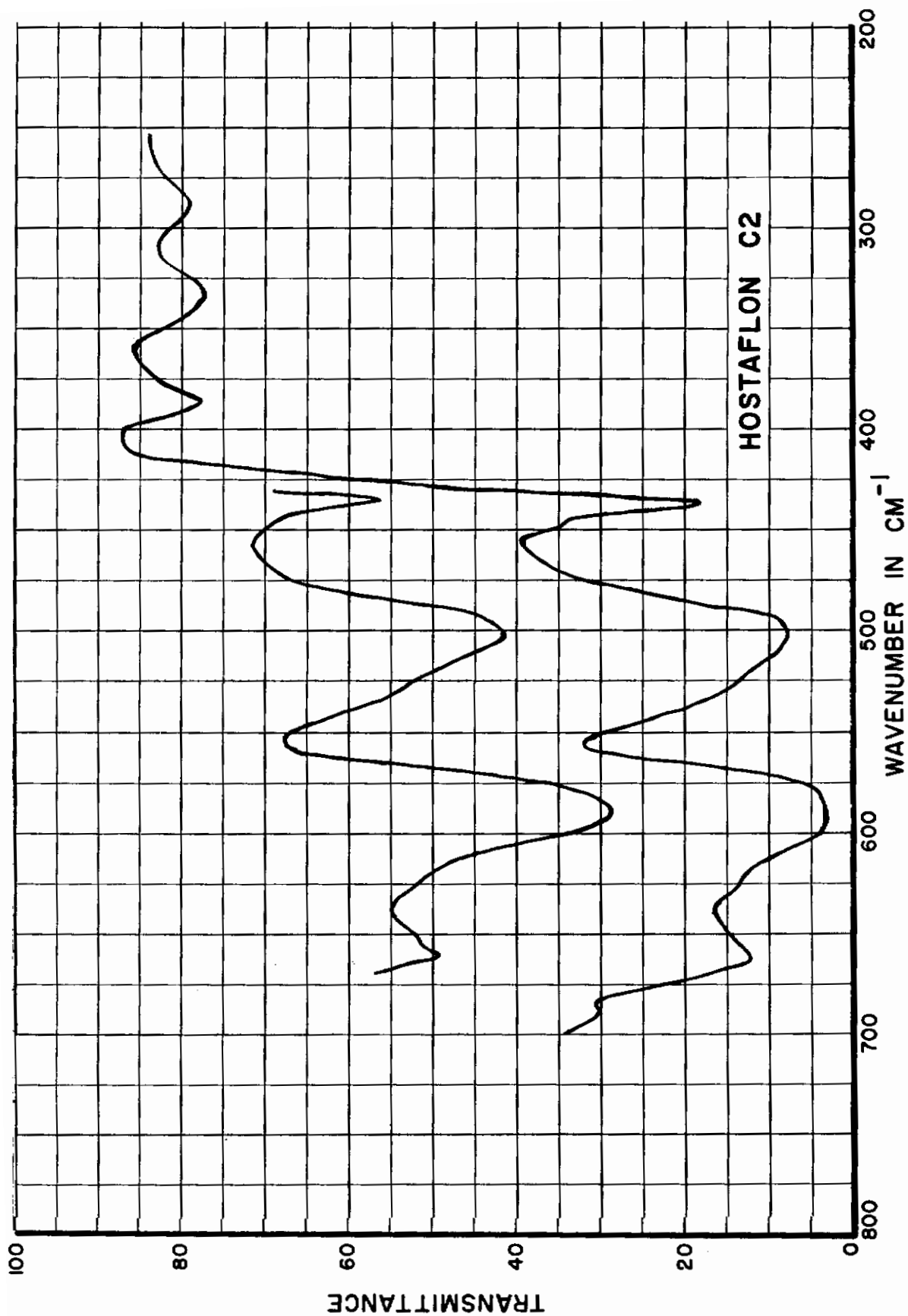


Figure 38. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Hostafilon C2 (Polychlorotrifluoroethylene)  
Recorded as a film approximately 0.04 mm in thickness (lower curve: linear absorbance; total ordinate: 2)

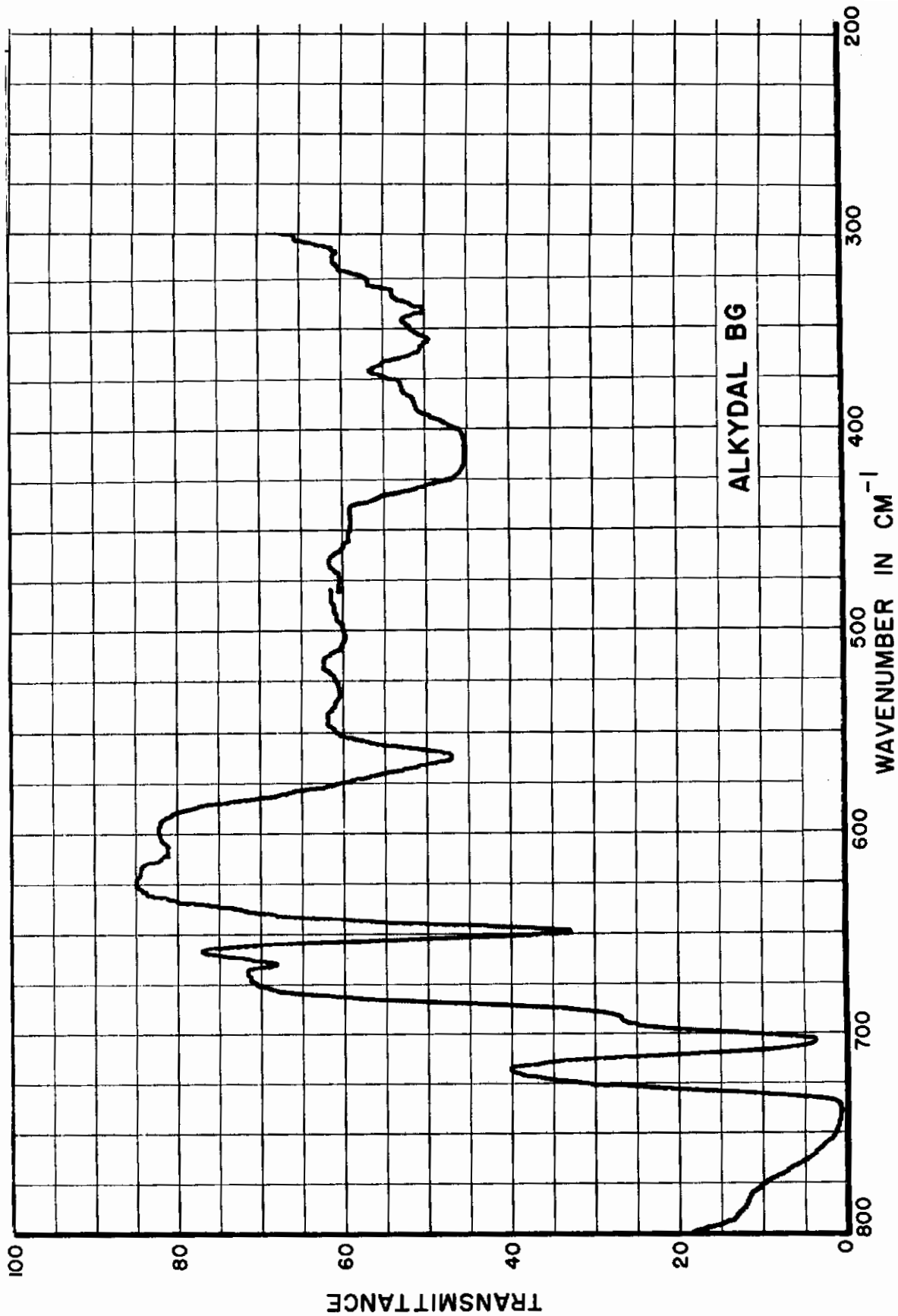


Figure 39. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Alkydal BG (Phthalic Acid Polyester; Oil-free)  
Recorded as a film

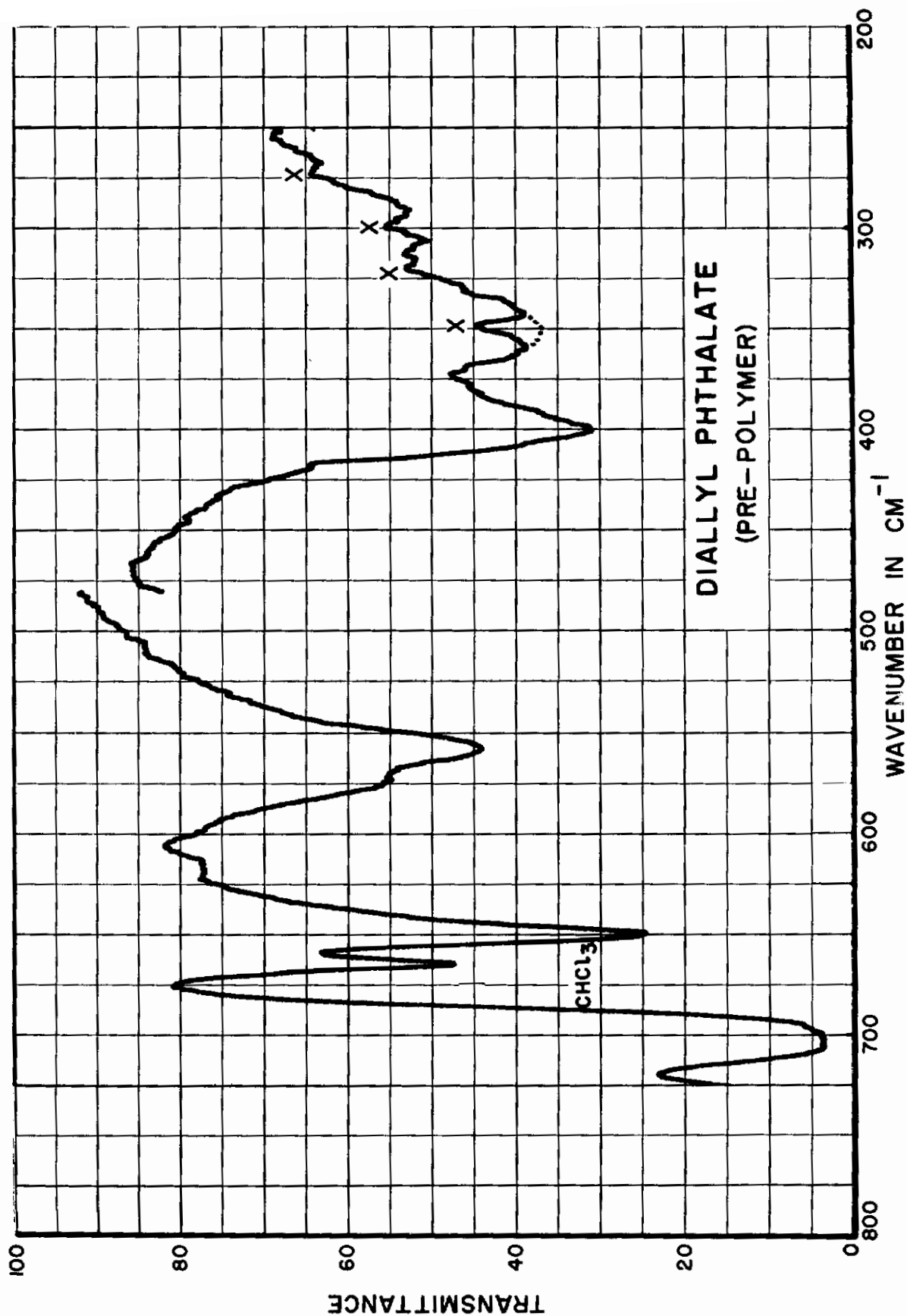


Figure 40. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Diallyl Phthalate (Prepolymer)  
Recorded as a film from a chloroform solution

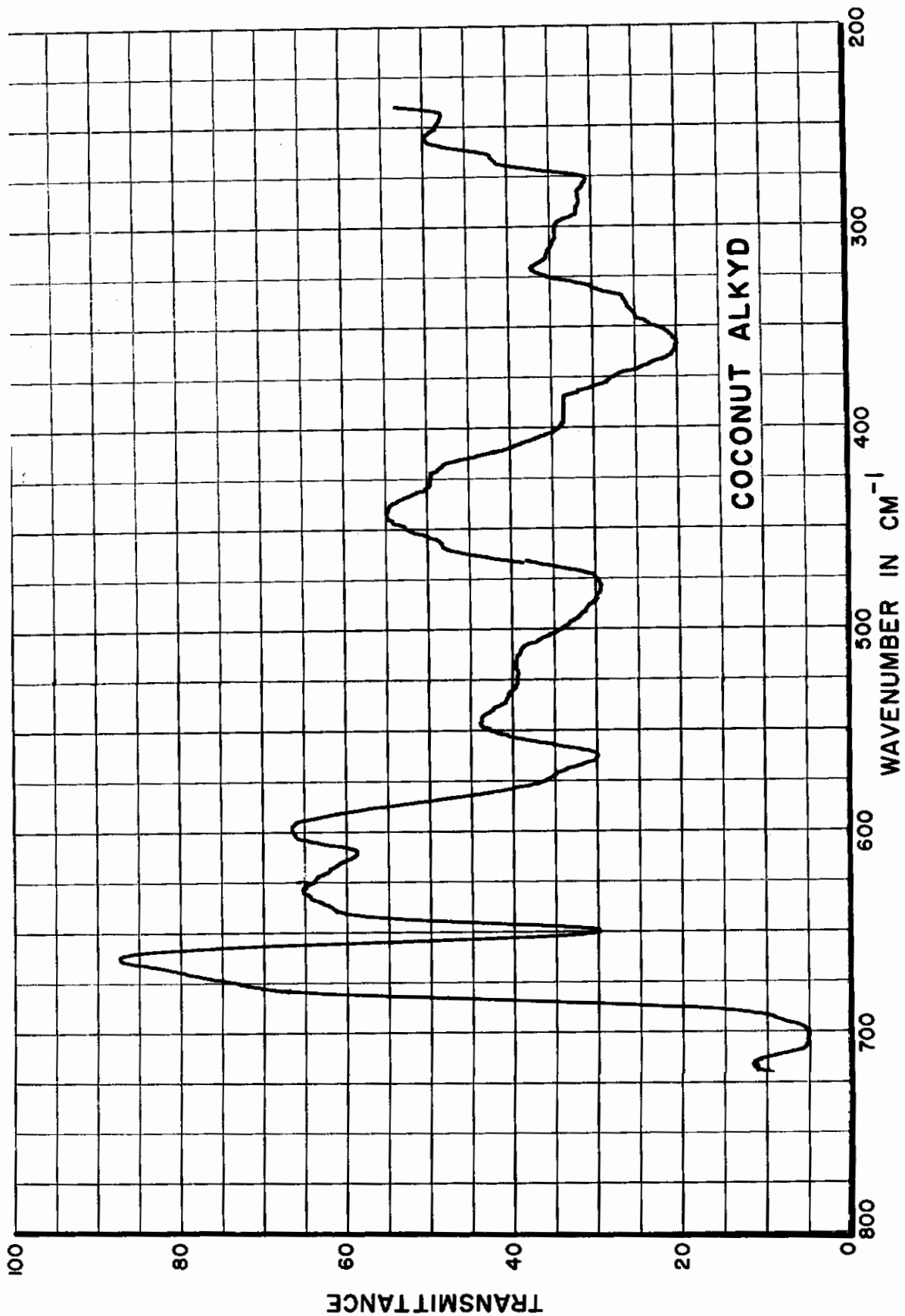


Figure 41. - Infrared Spectrum from 725 - 250  $\text{cm}^{-1}$  of an Alkyd Resin, 42% Coconut Oil.  
(Alftalat 458 S)

Recorded as a film

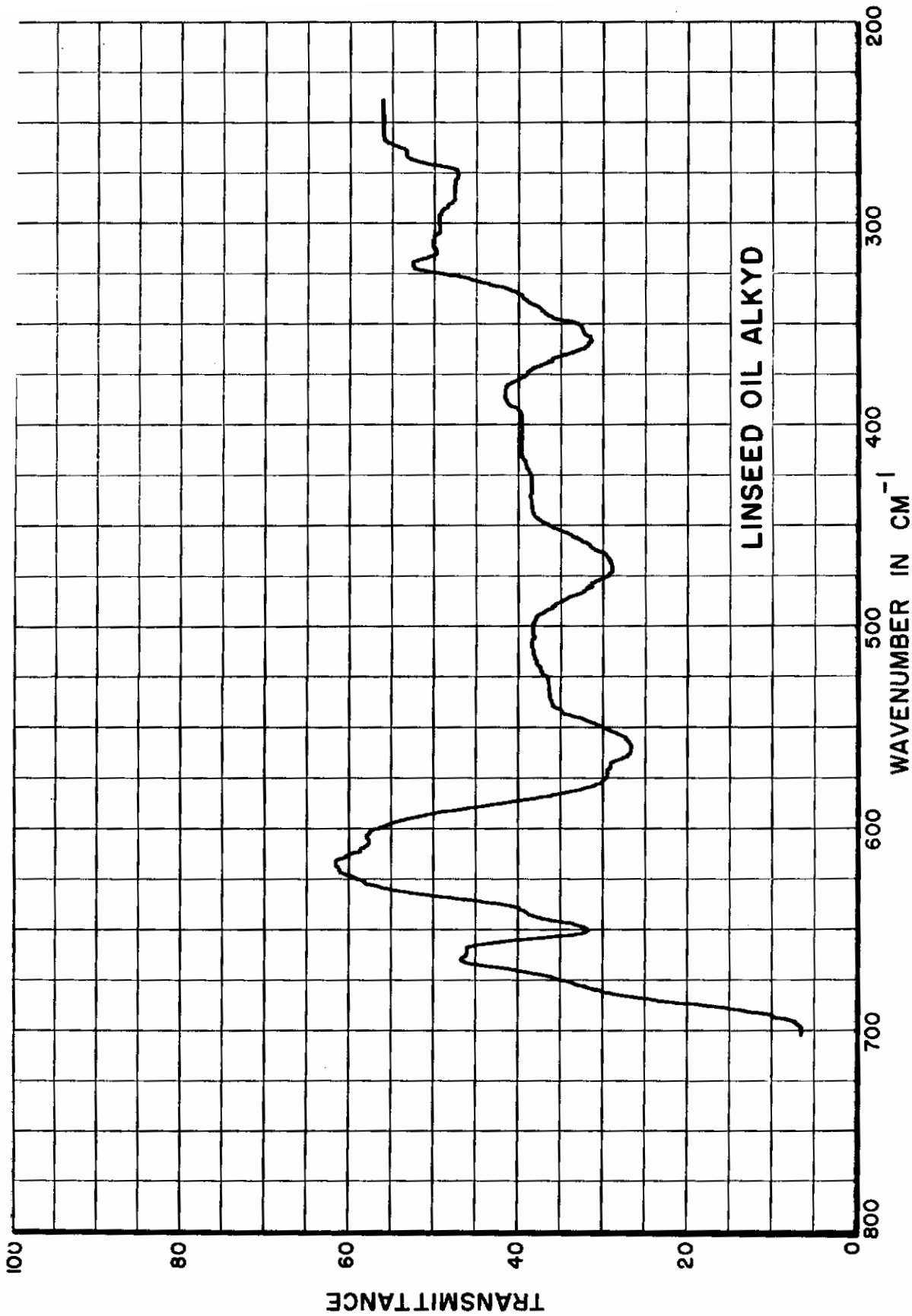


Figure 42. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Linseed Oil Alkyd Resin (Jaegalyd TAP)  
Recorded as a film

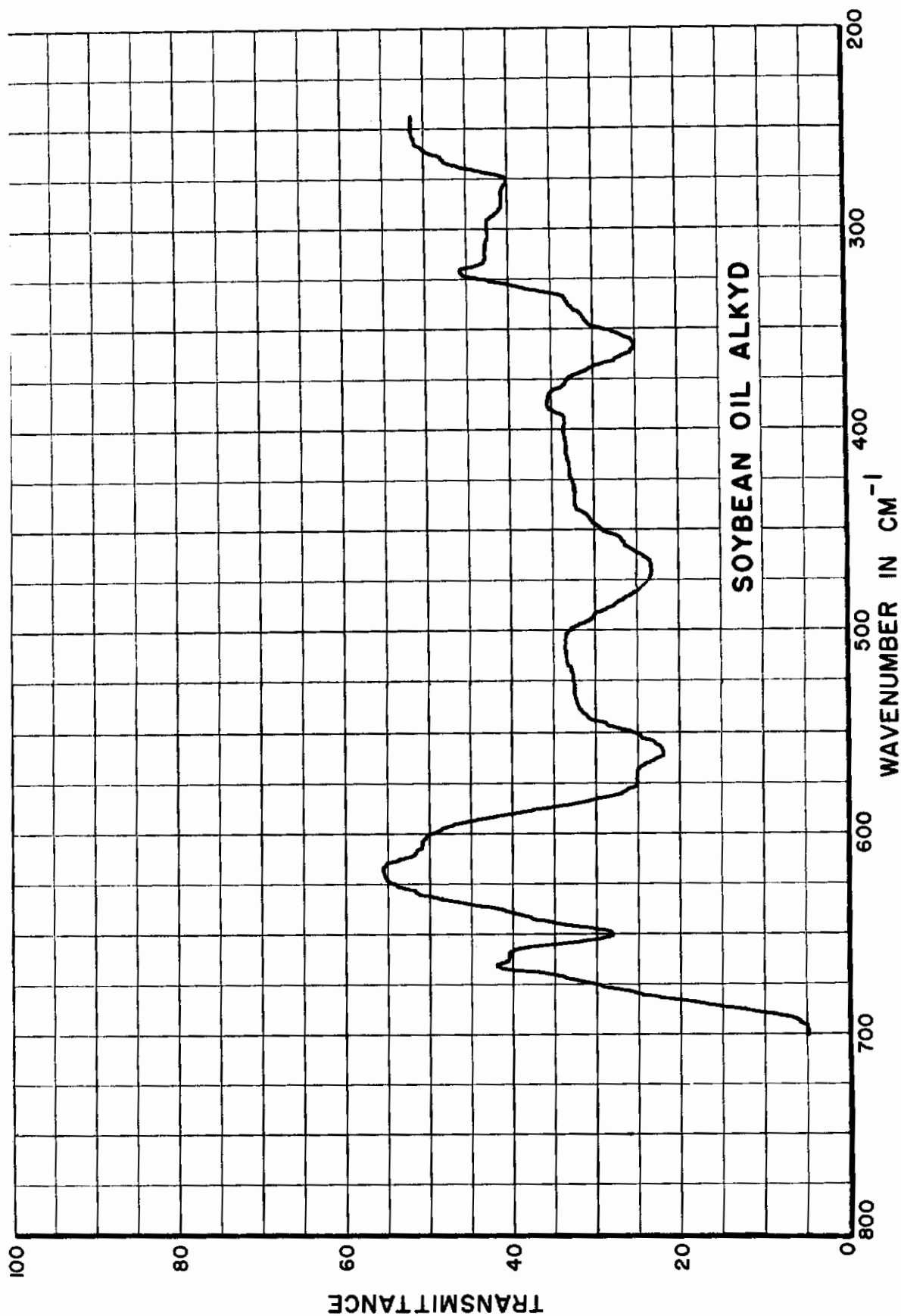


Figure 43. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Soybean Oil Alkyd Resin (Alkydal T Extra)  
Recorded as a film



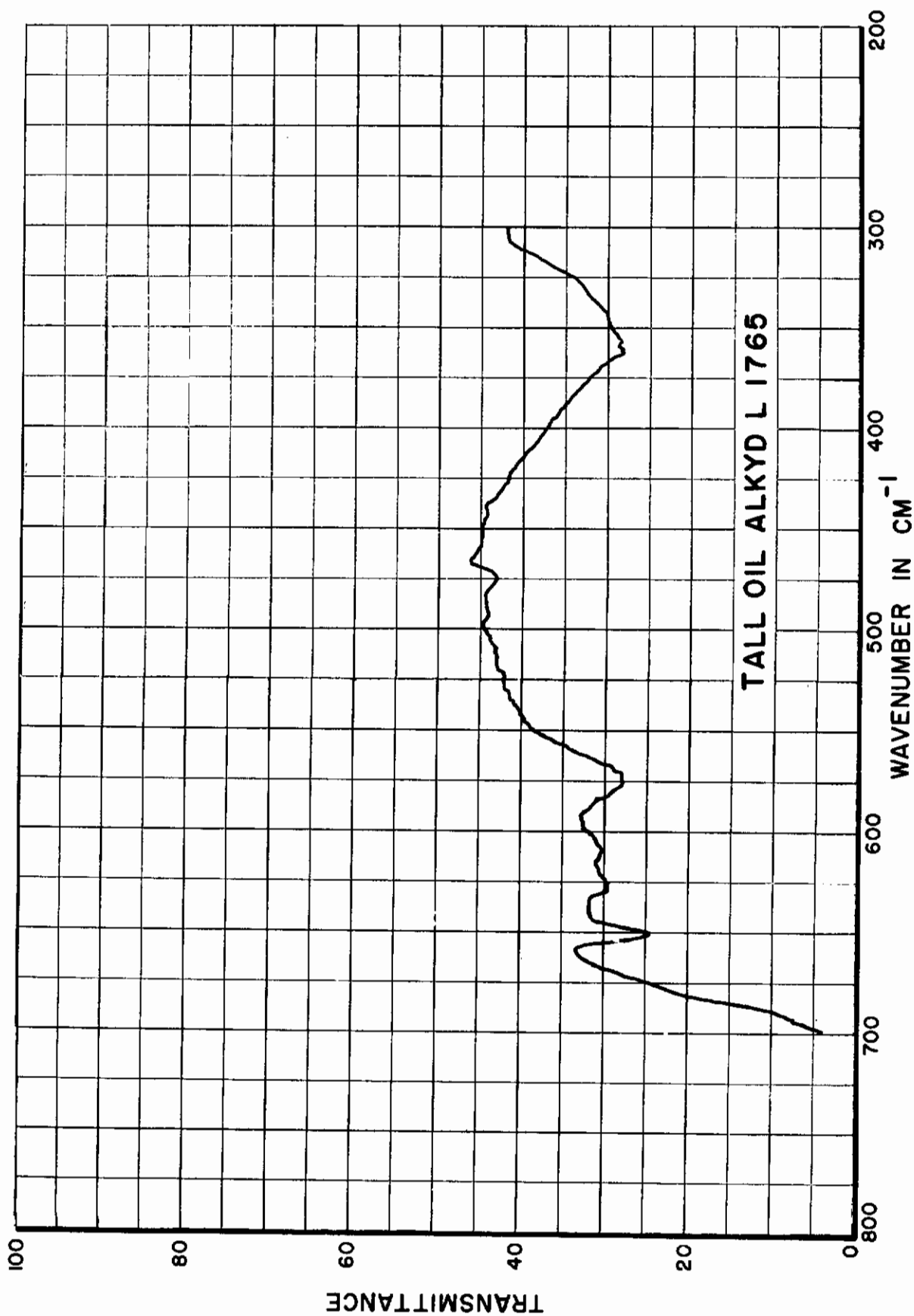


Figure 44. - Infrared Spectrum from 700 - 300  $\text{cm}^{-1}$  of Alkyd Resin with 80% Tall Oil (Tall Oil Alkyd L 1765)

Recorded as a film

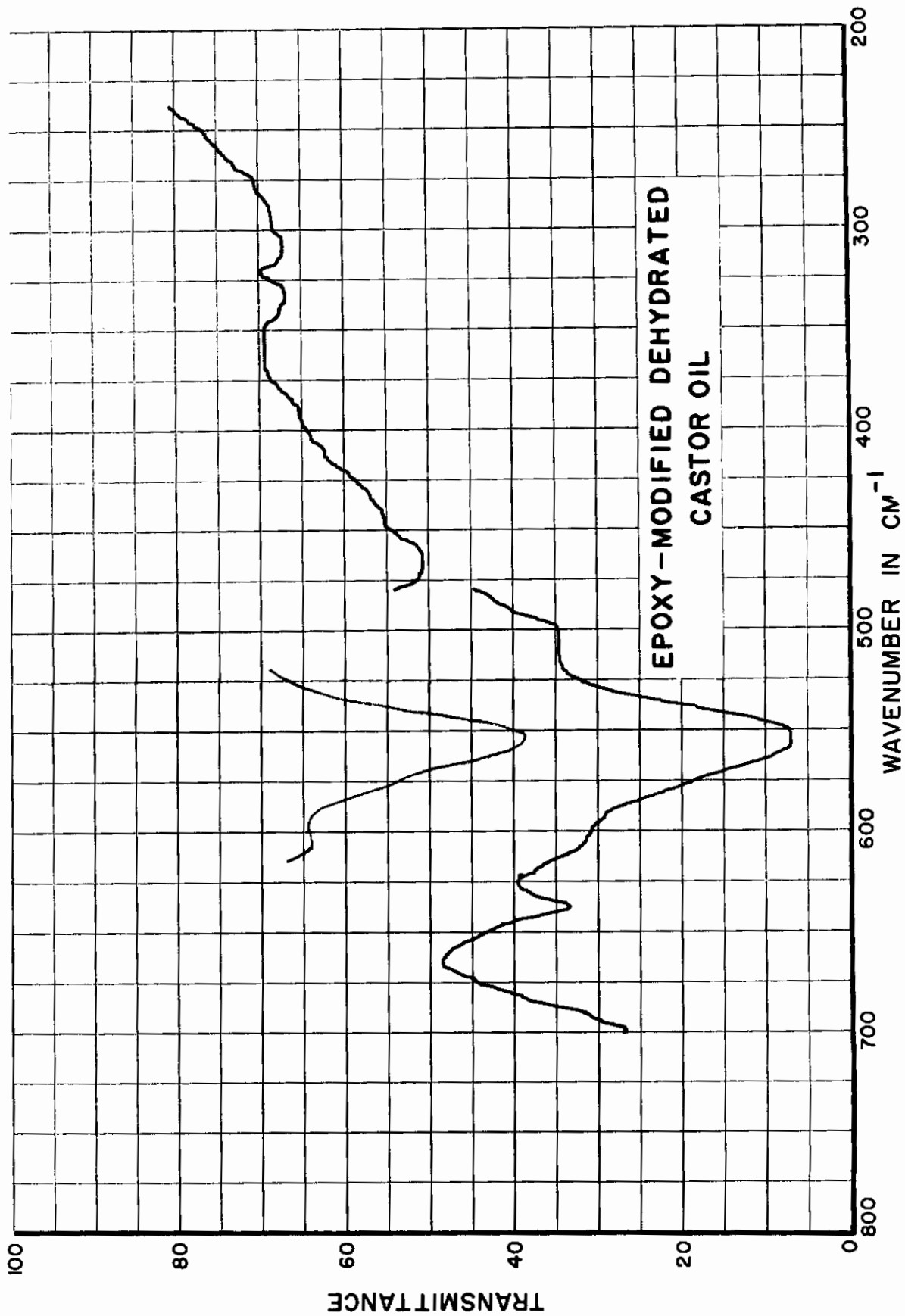


Figure 45. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Epoxy-Modified Dehydrated Castor Oil.  
Recorded as a film

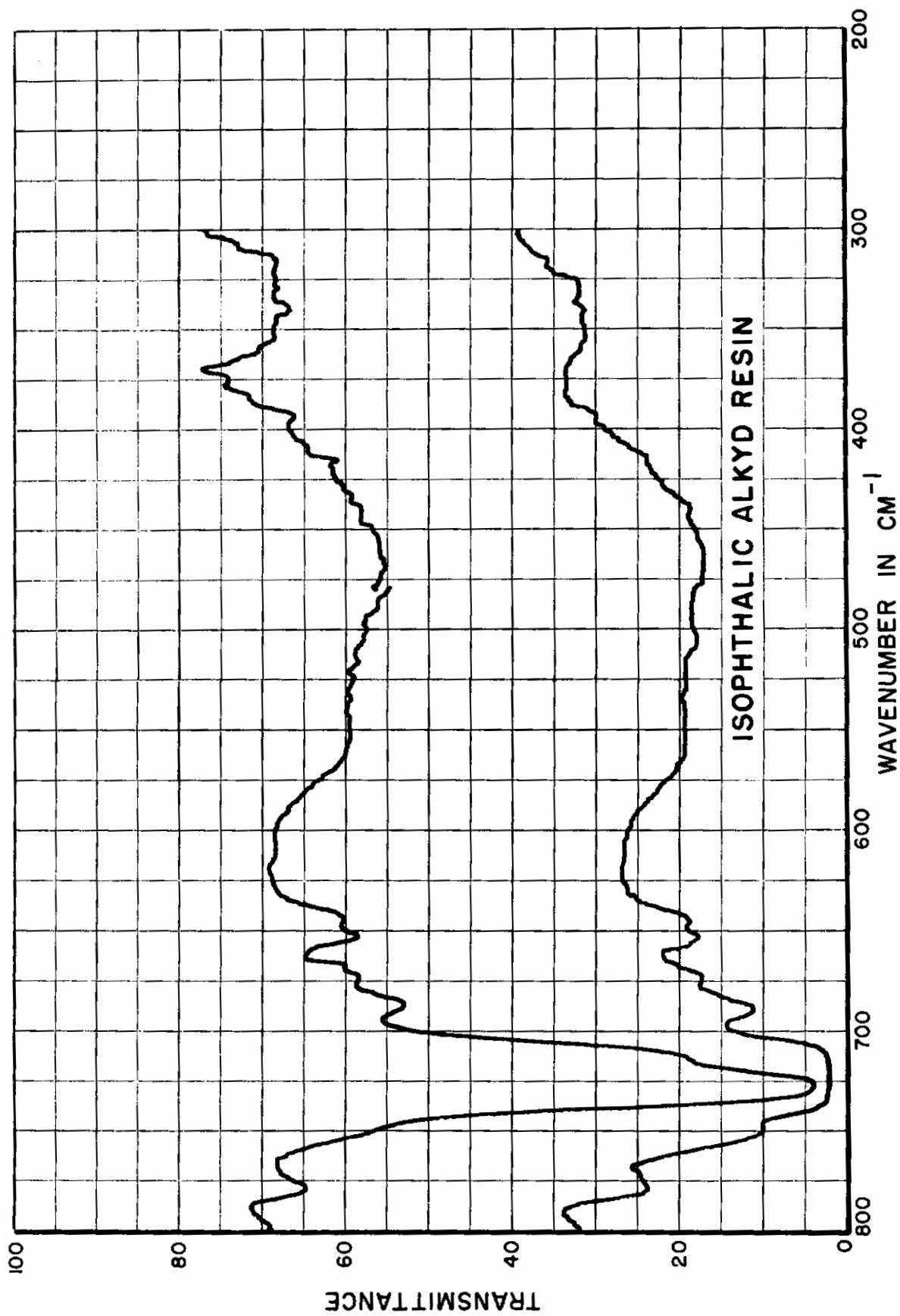


Figure 46. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Isophthalic Alkyd Resin with Soybean Oil (Jaegalyd) Recorded as a melted film

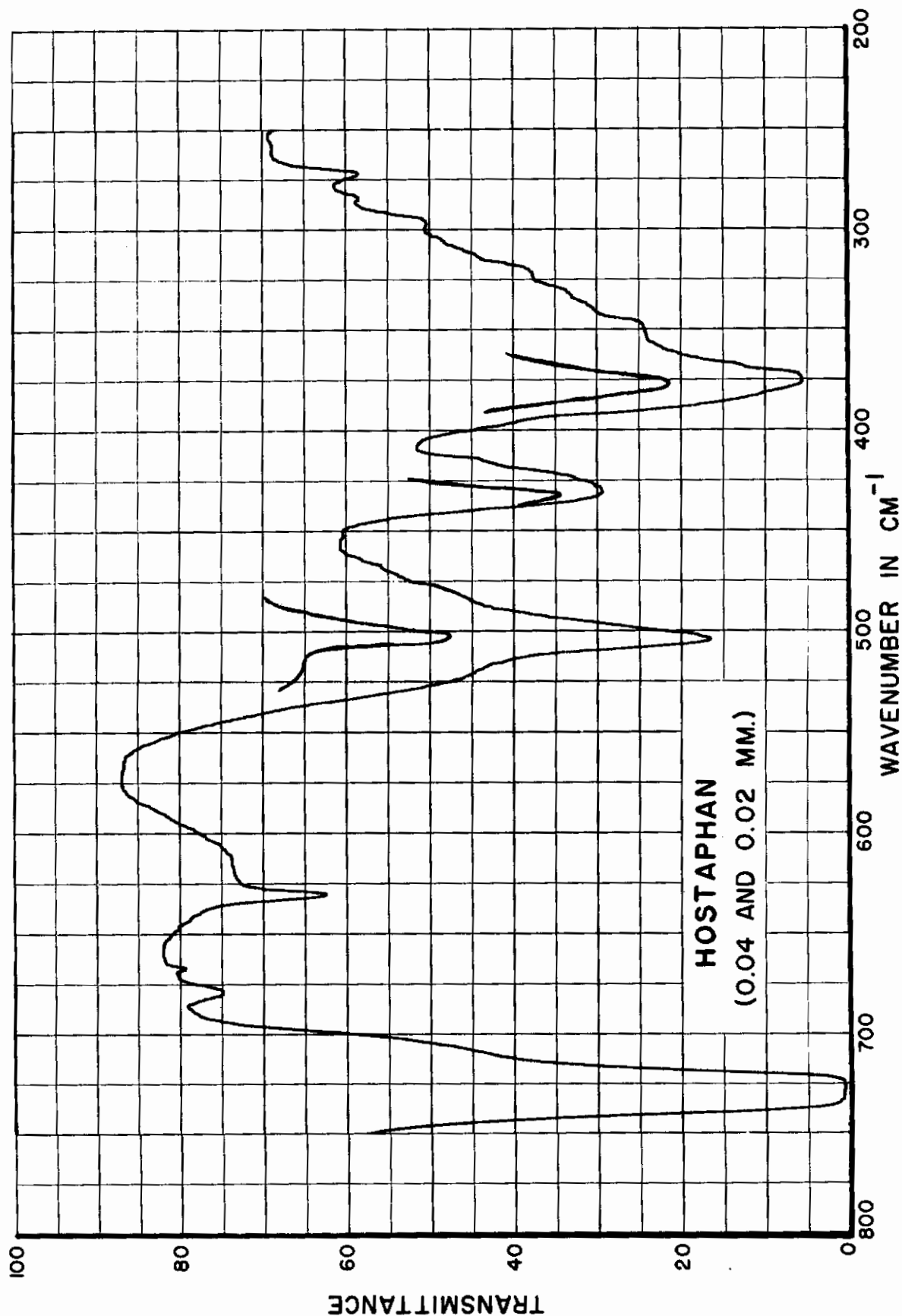


Figure 47. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Hostaphan (Ethylene Glycol-Terephthalic Acid, Polyester)  
Recorded as films 0.02 mm and 0.04 mm in pathlength. The band at 666 cm<sup>-1</sup> attributed to atmospheric absorption

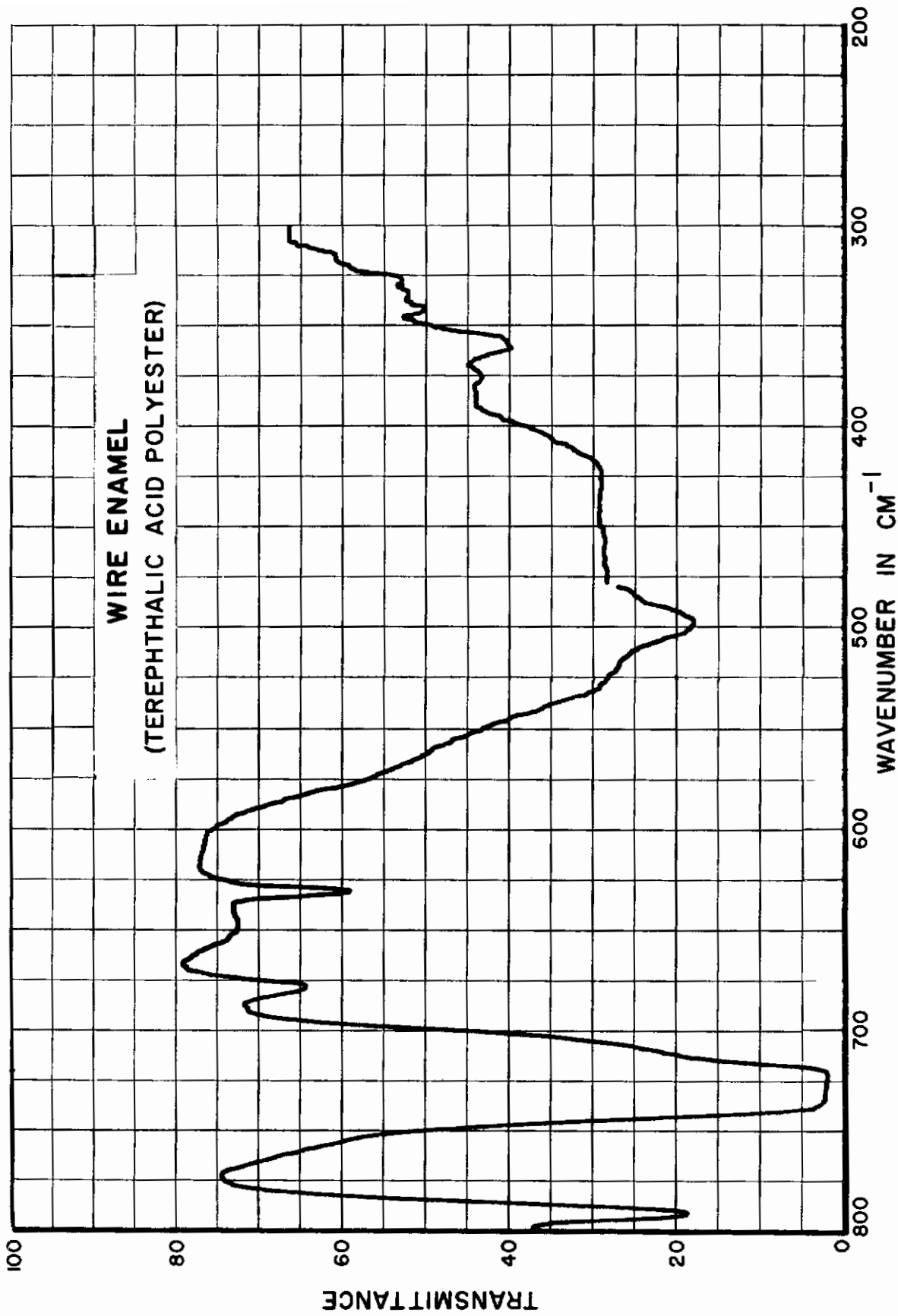


Figure 48. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Wire Enamel on Base of Terephthalic Acid Polyester  
Recorded as a film

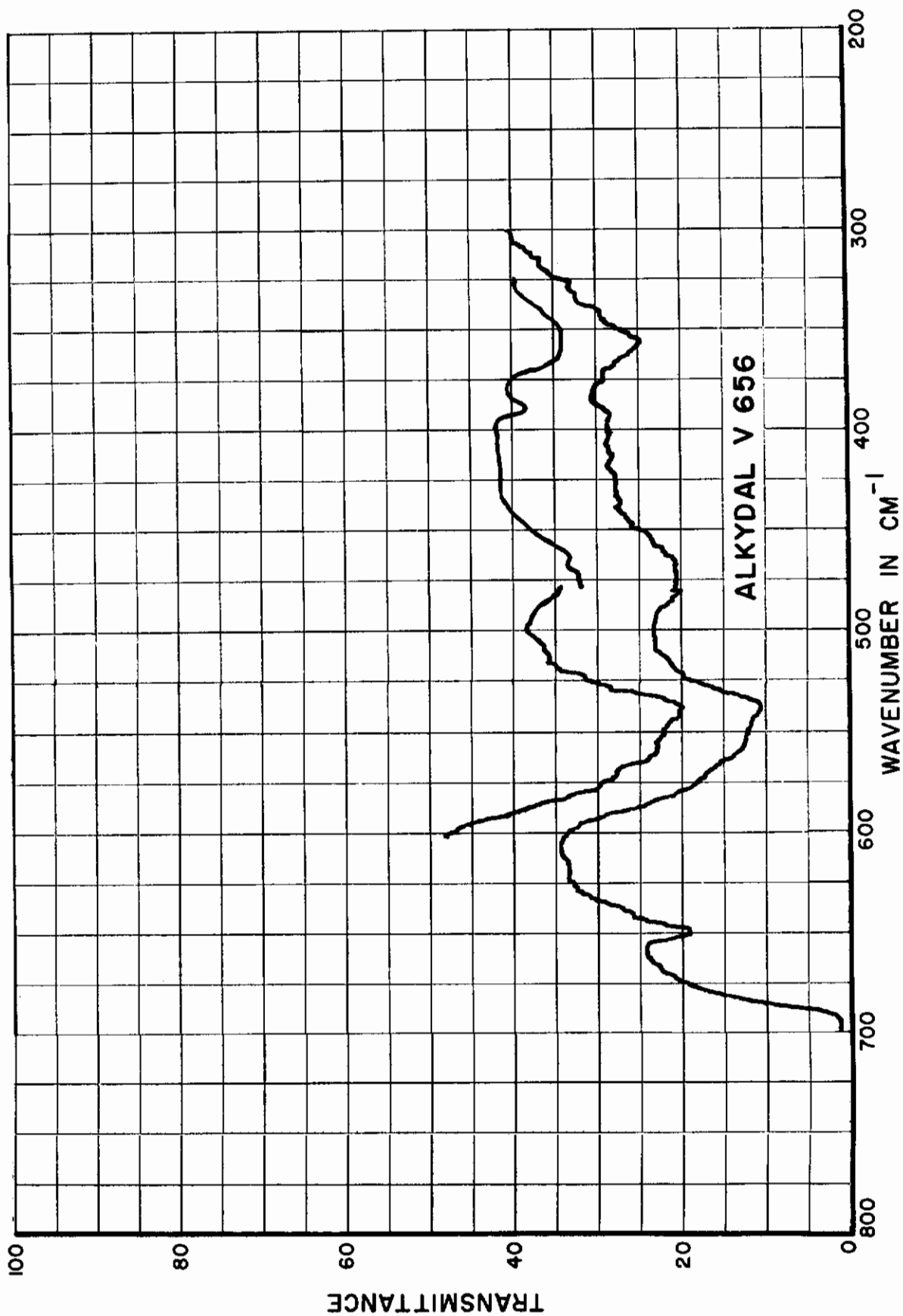


Figure 49. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Alkydal V 656 (Sytrenated Alkyd Resin)  
Recorded as a melted film approximately 0.11 mm in thickness

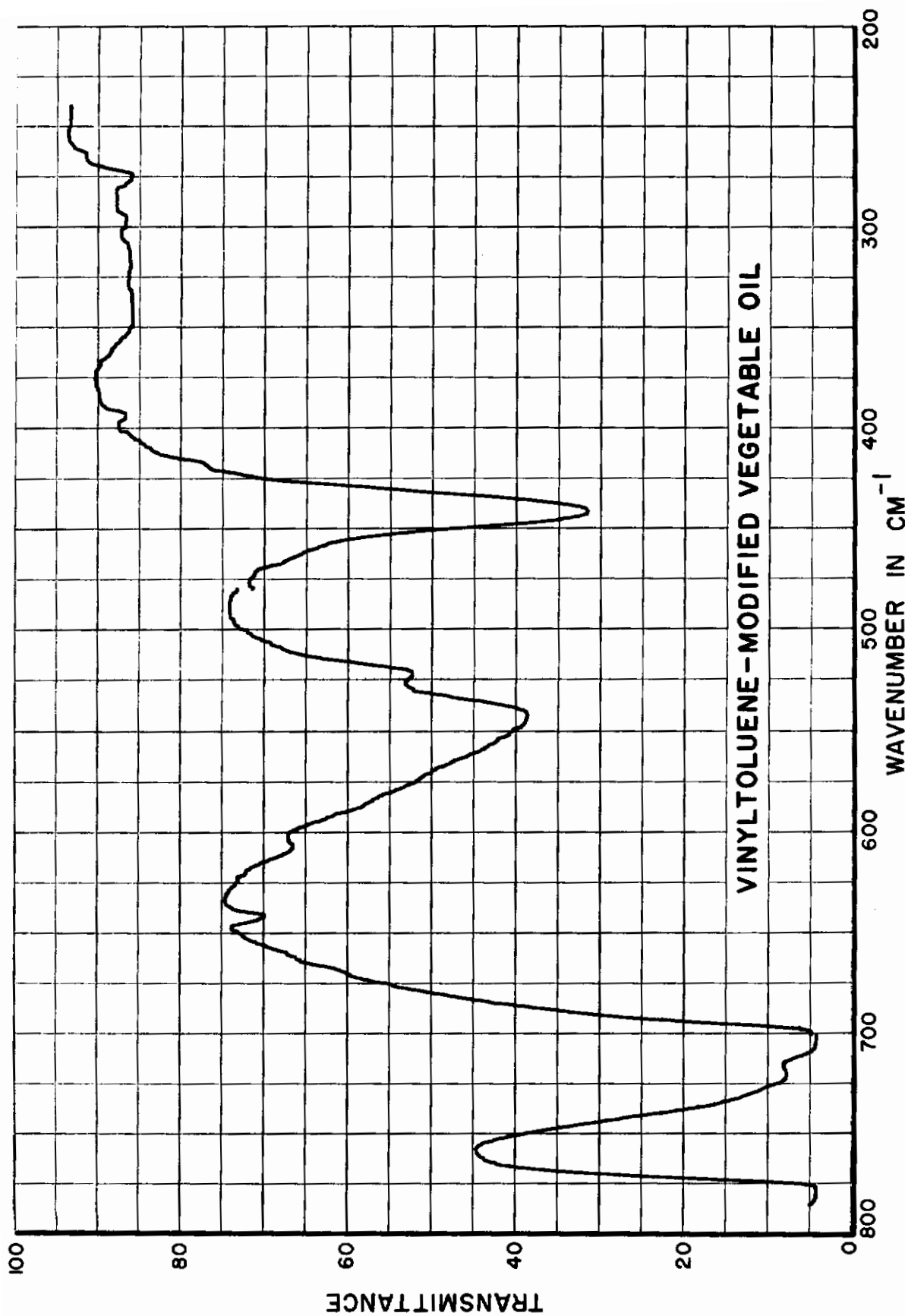


Figure 50. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Vinyltoluene-Modified Vegetable Oil  
(Setal 5000 SS-60)

Recorded as a film

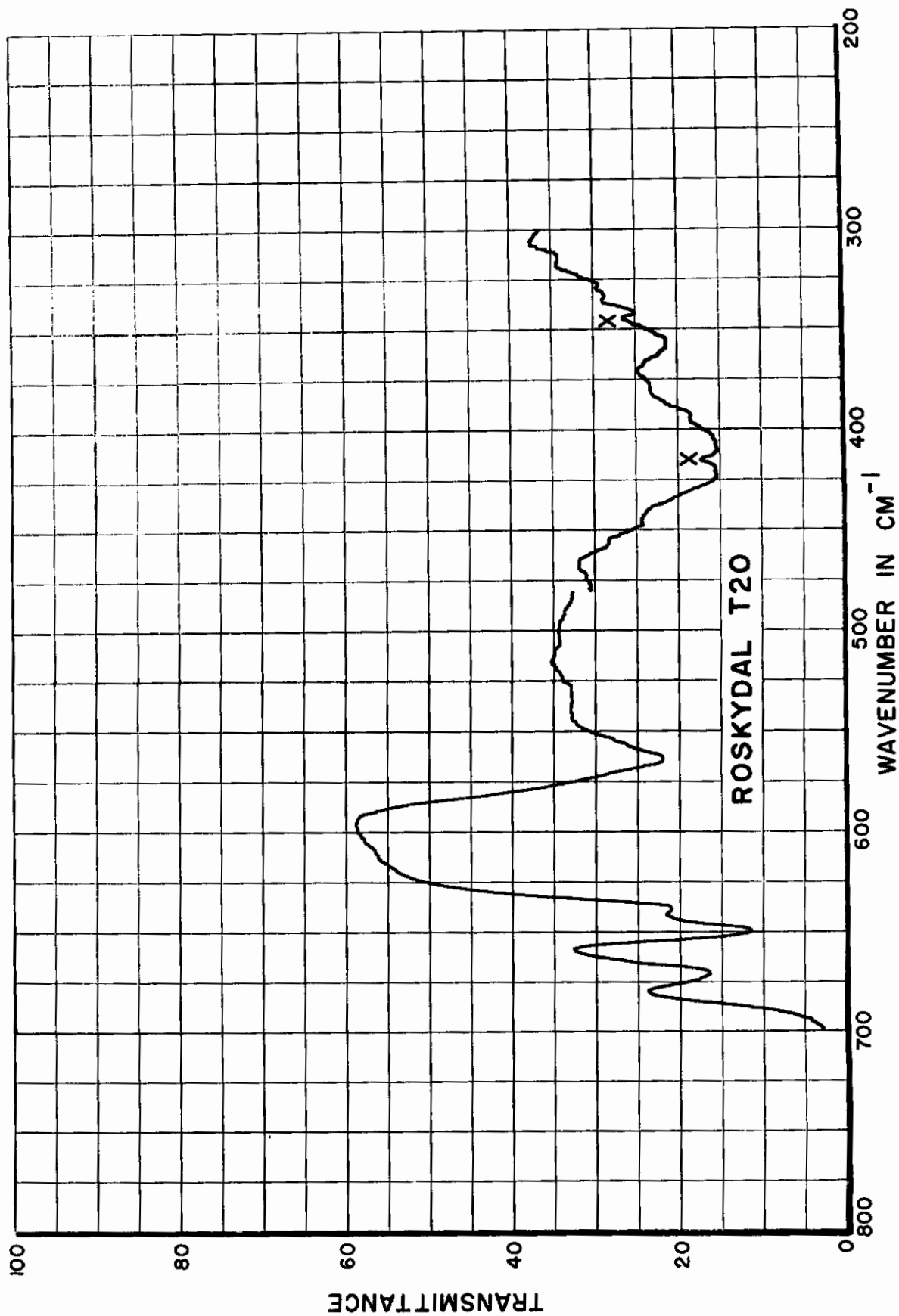


Figure 51. - Infrared Spectrum from 700 - 300  $\text{cm}^{-1}$  of Roskydal T 20 (Unsaturated Polyester Resin)  
Recorded as a melted film



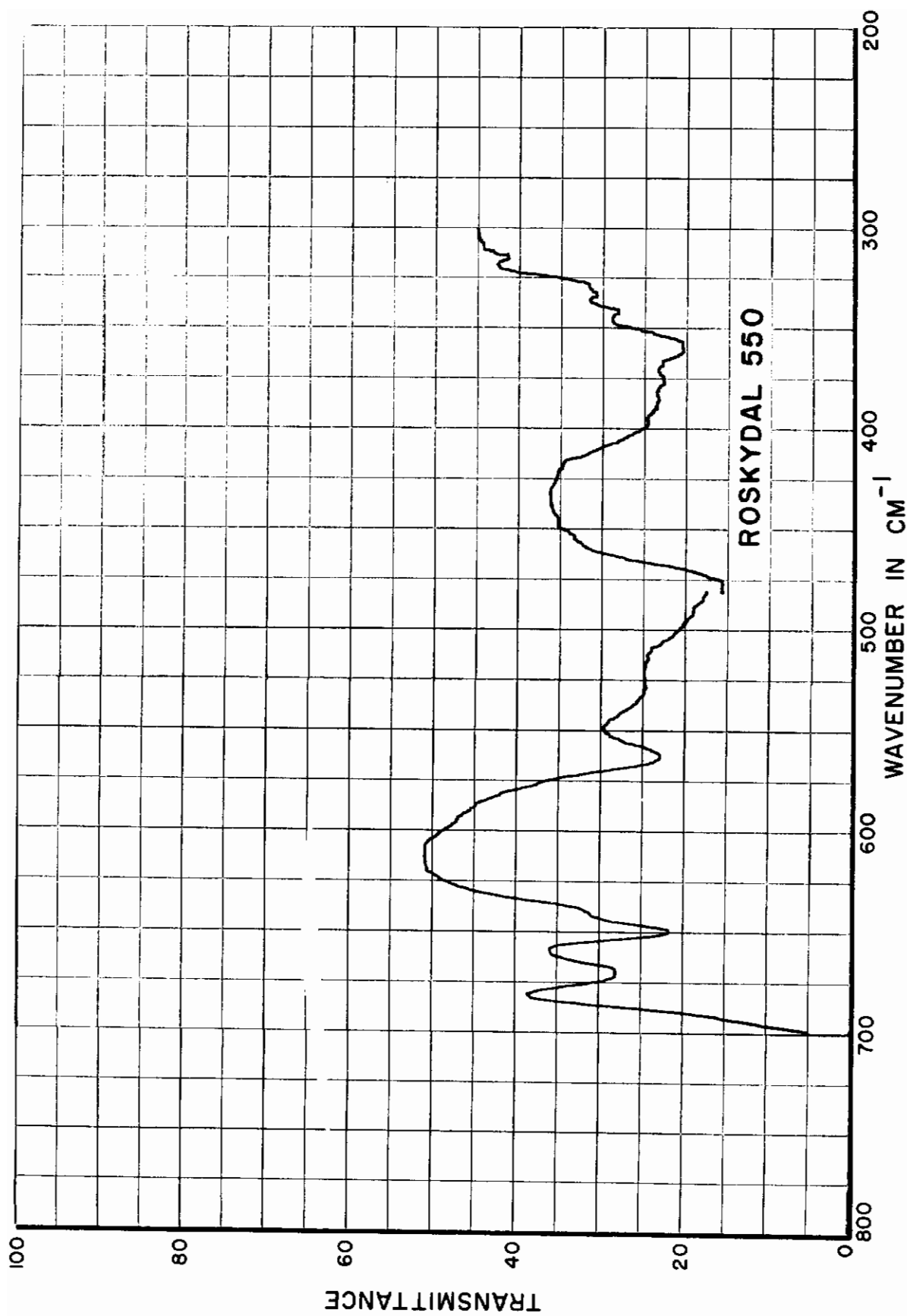


Figure 52. - Infrared Spectrum from 700 - 300  $\text{cm}^{-1}$  of Roskydal 550 (Unsaturated Polyester Resin)  
Recorded as a melted film

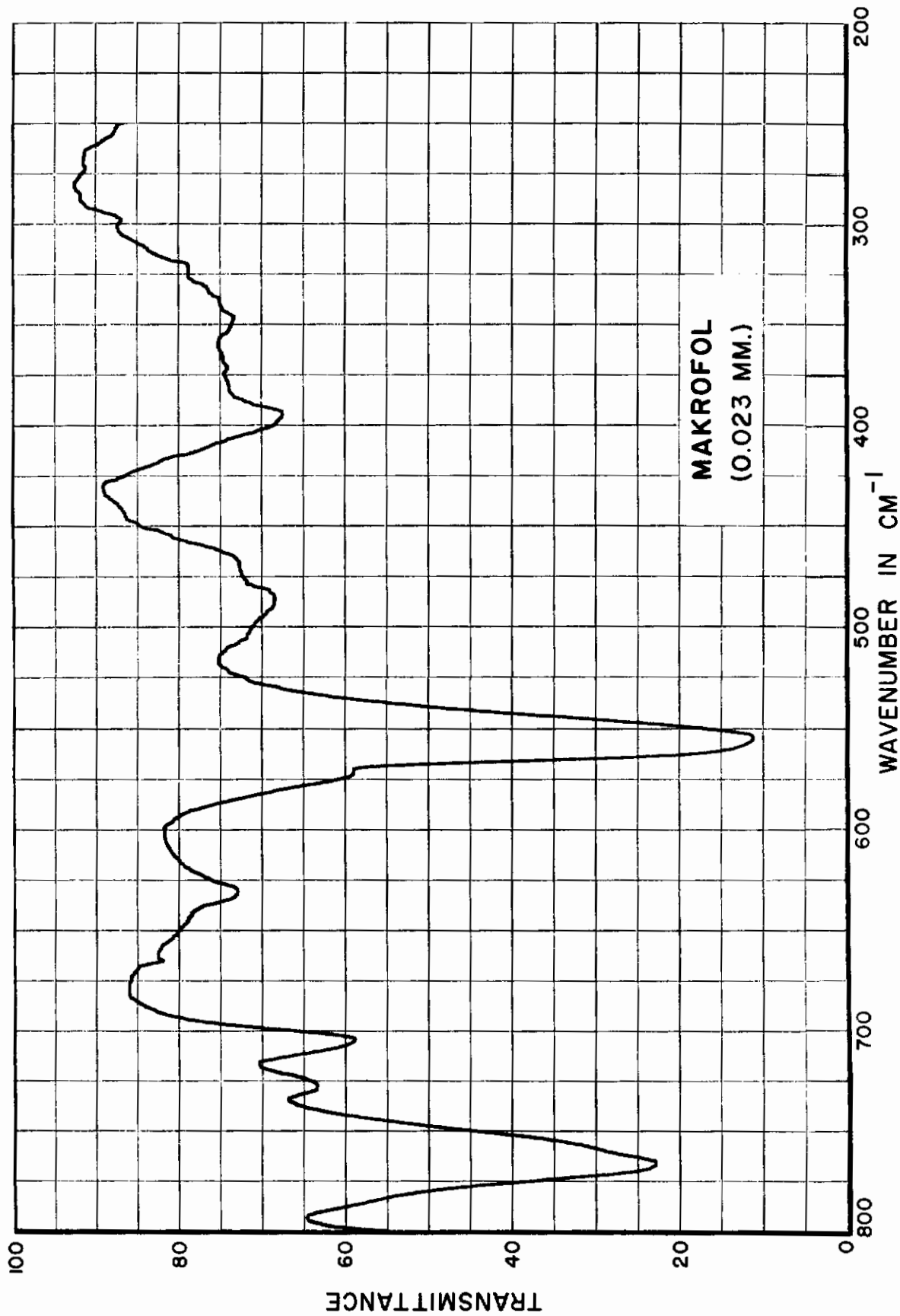


Figure 53. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Makrofol (Polycarbonate on Base of "Bisphenol A")  
Recorded as a film, 0.023 mm in thickness

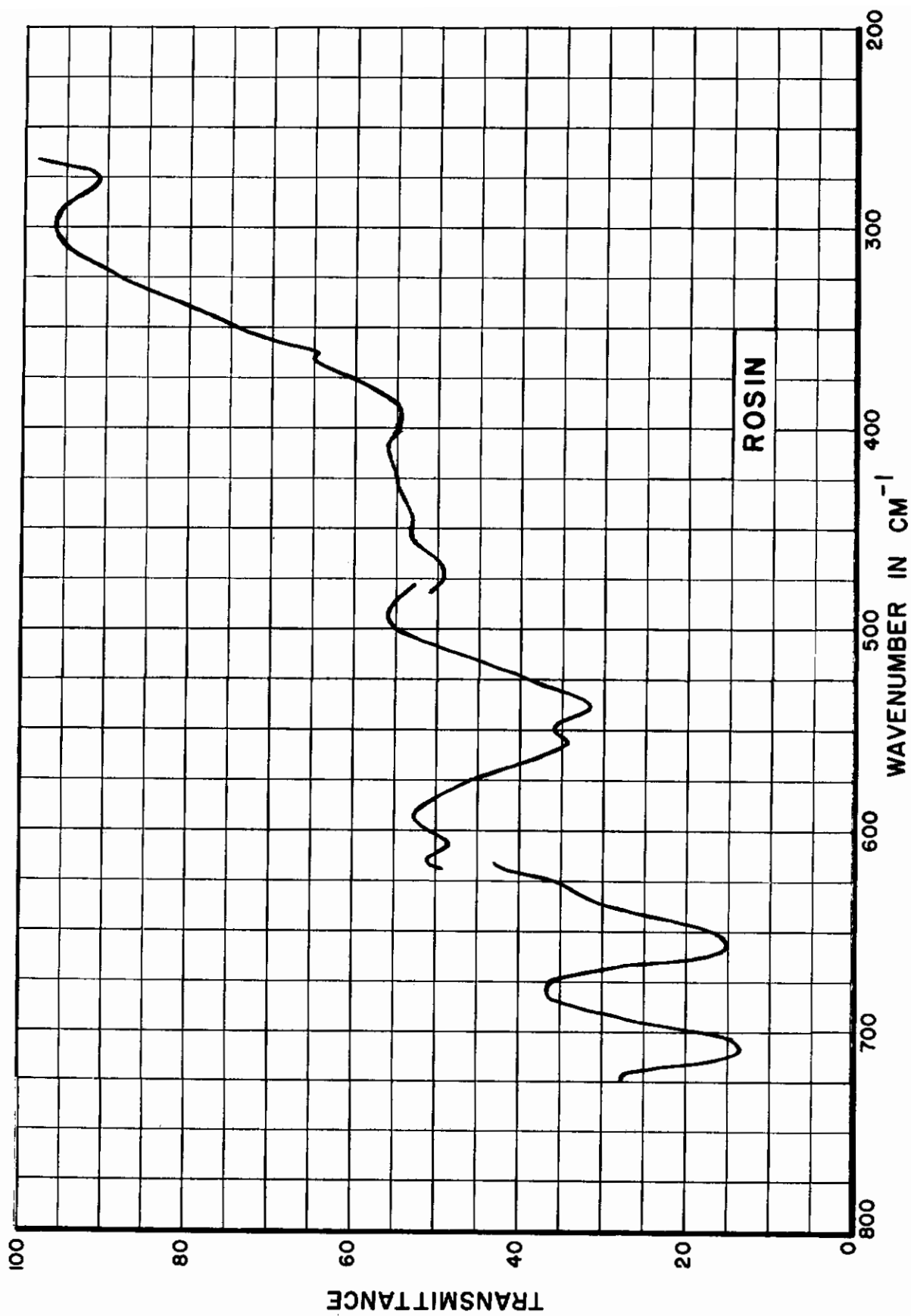


Figure 54. - Infrared Spectrum from 725 - 275 cm<sup>-1</sup> of Rosin (Abietic Acid)  
Recorded as a film, prepared from chloroform solution

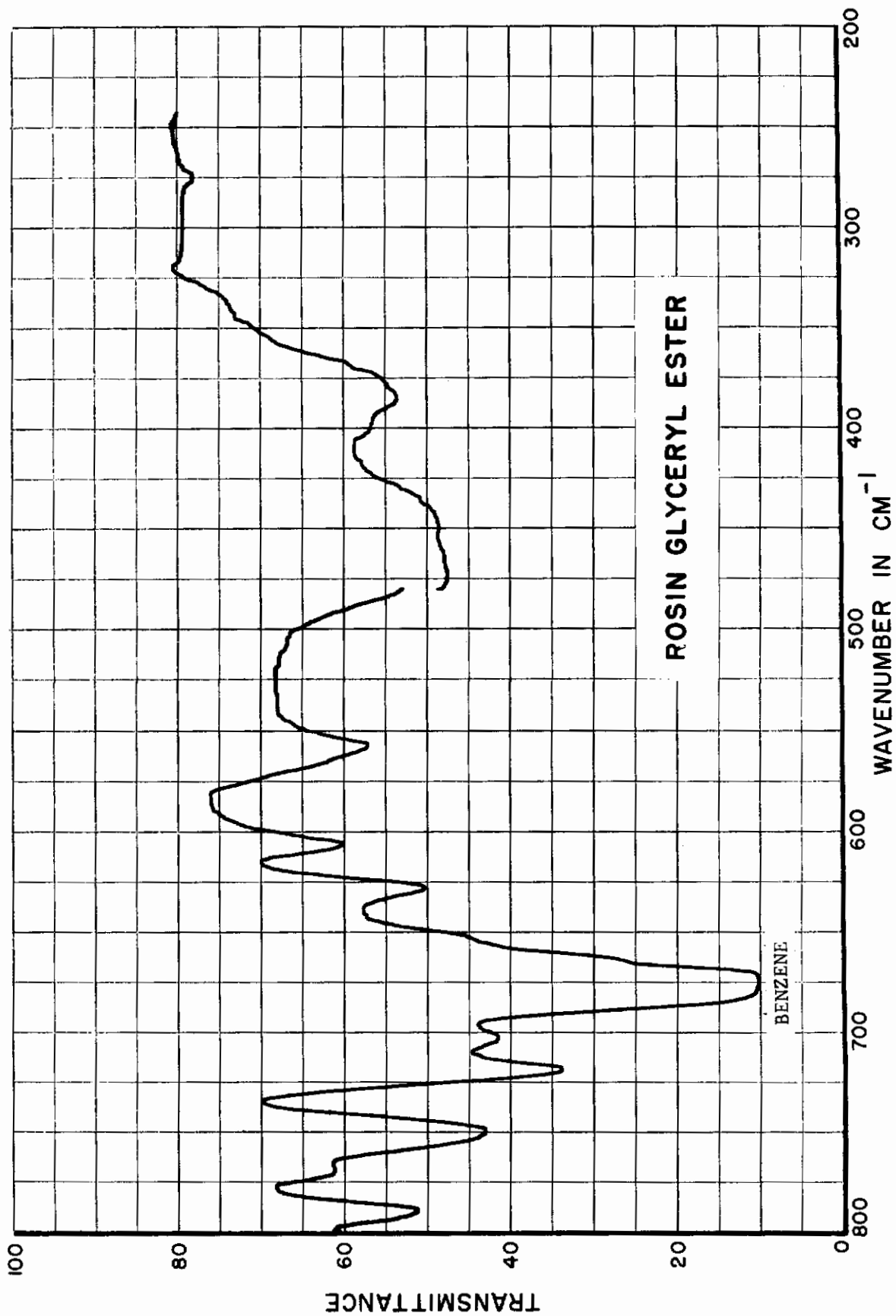


Figure 55. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Rosin Glyceryl Ester (Gamesco G) Recorded as a film, prepared from benzene solution

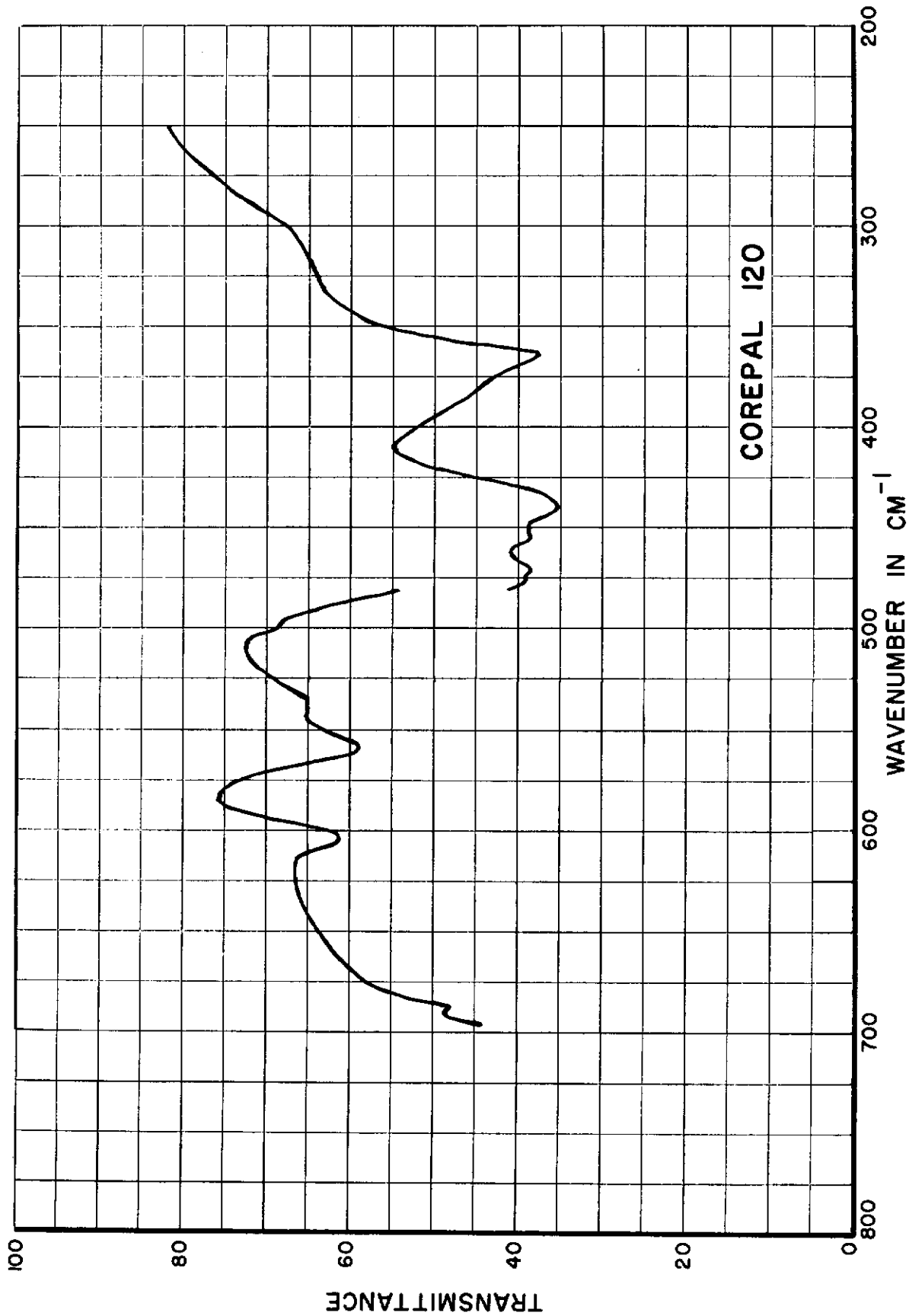


Figure 56. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Corepal 120 (Maleinate Resin)  
Recorded as a film, prepared from chloroform solution

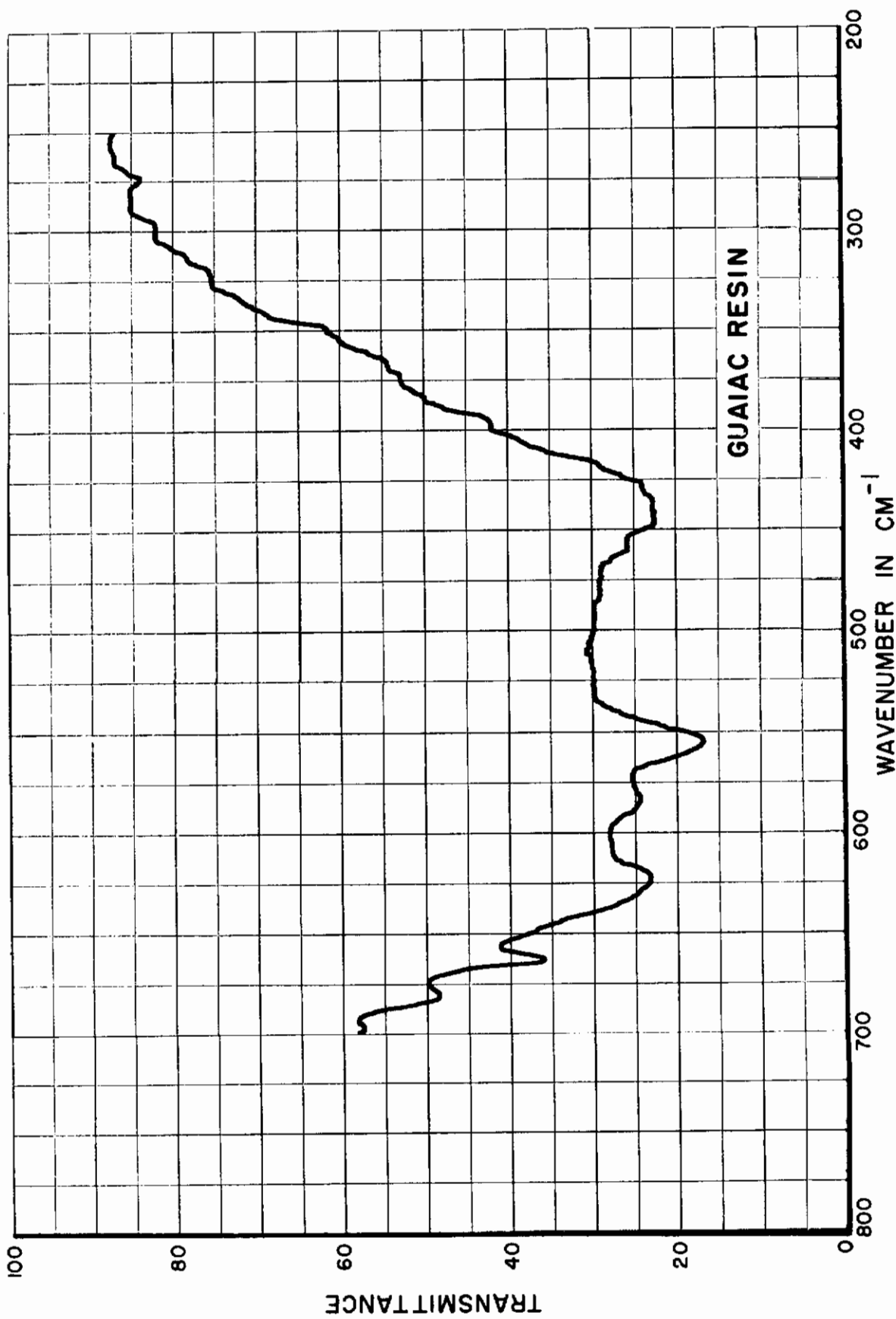


Figure 57. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Guaiac Resin (a Mixture of 70% Guaiaconic Acid and 30% Other Acid and Neutral Compounds)

Recorded as a film, prepared from chloroform solution. The band at 665 cm<sup>-1</sup> is probably due to chloroform

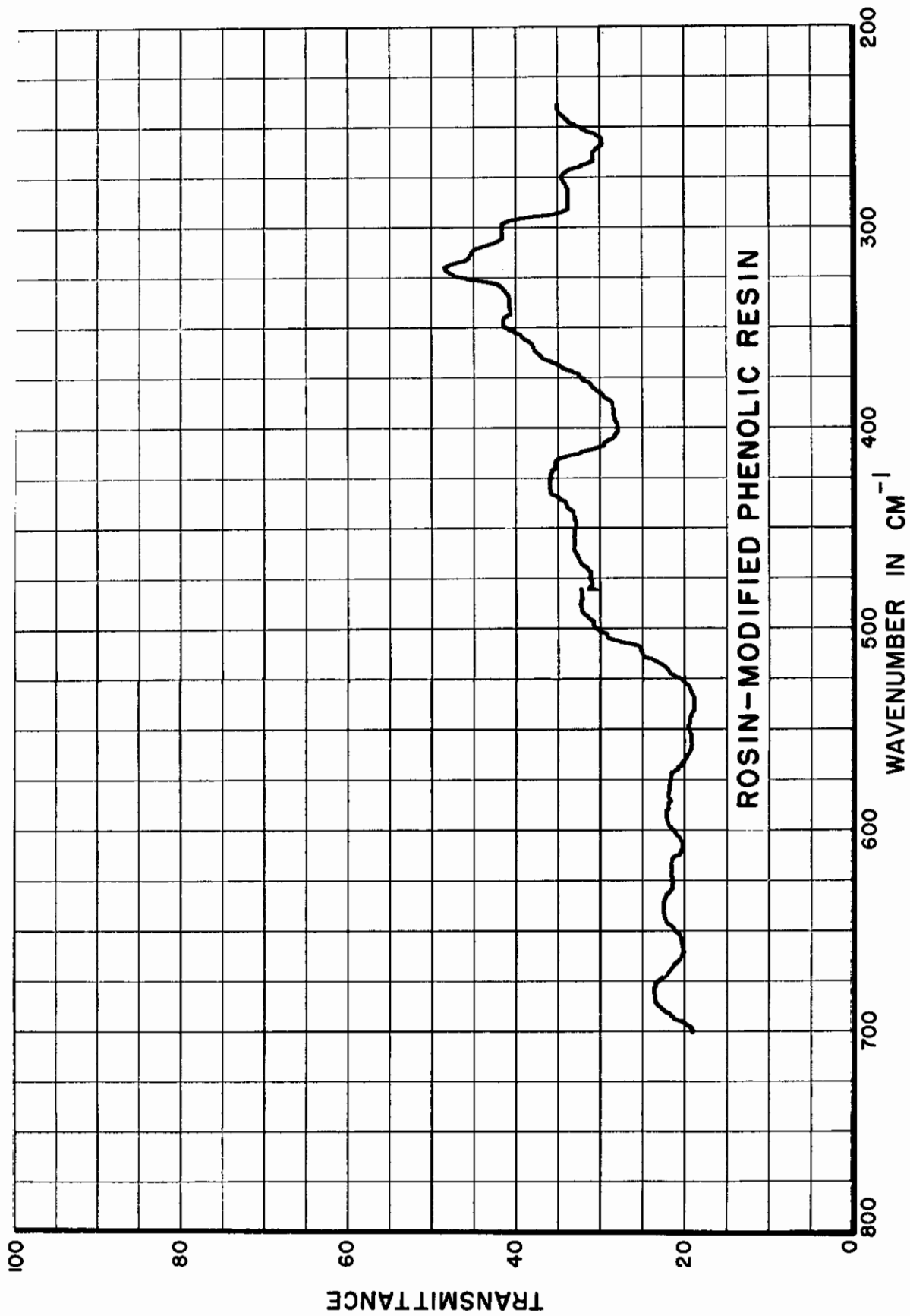


Figure 58. - Infrared Spectrum from 700 - 238 cm<sup>-1</sup> of Rosin-Modified Phenolic Resin (Mastolyn)  
Recorded as a film, prepared from n-butanol

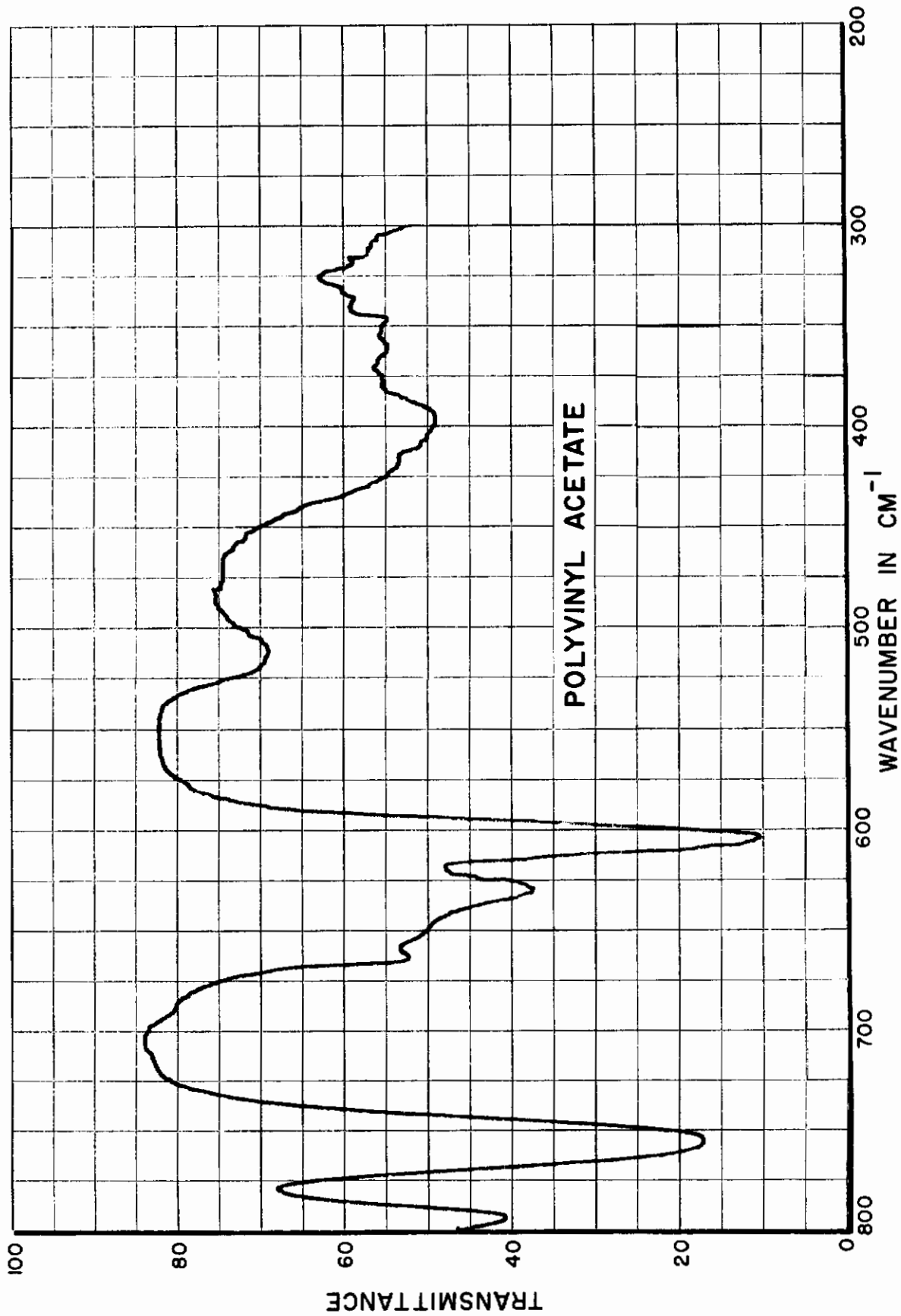


Figure 59. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Polyvinyl Acetate  
Recorded as a film, 0.20 mm in thickness, prepared  
from an isopropanol-water mixture (9:1)



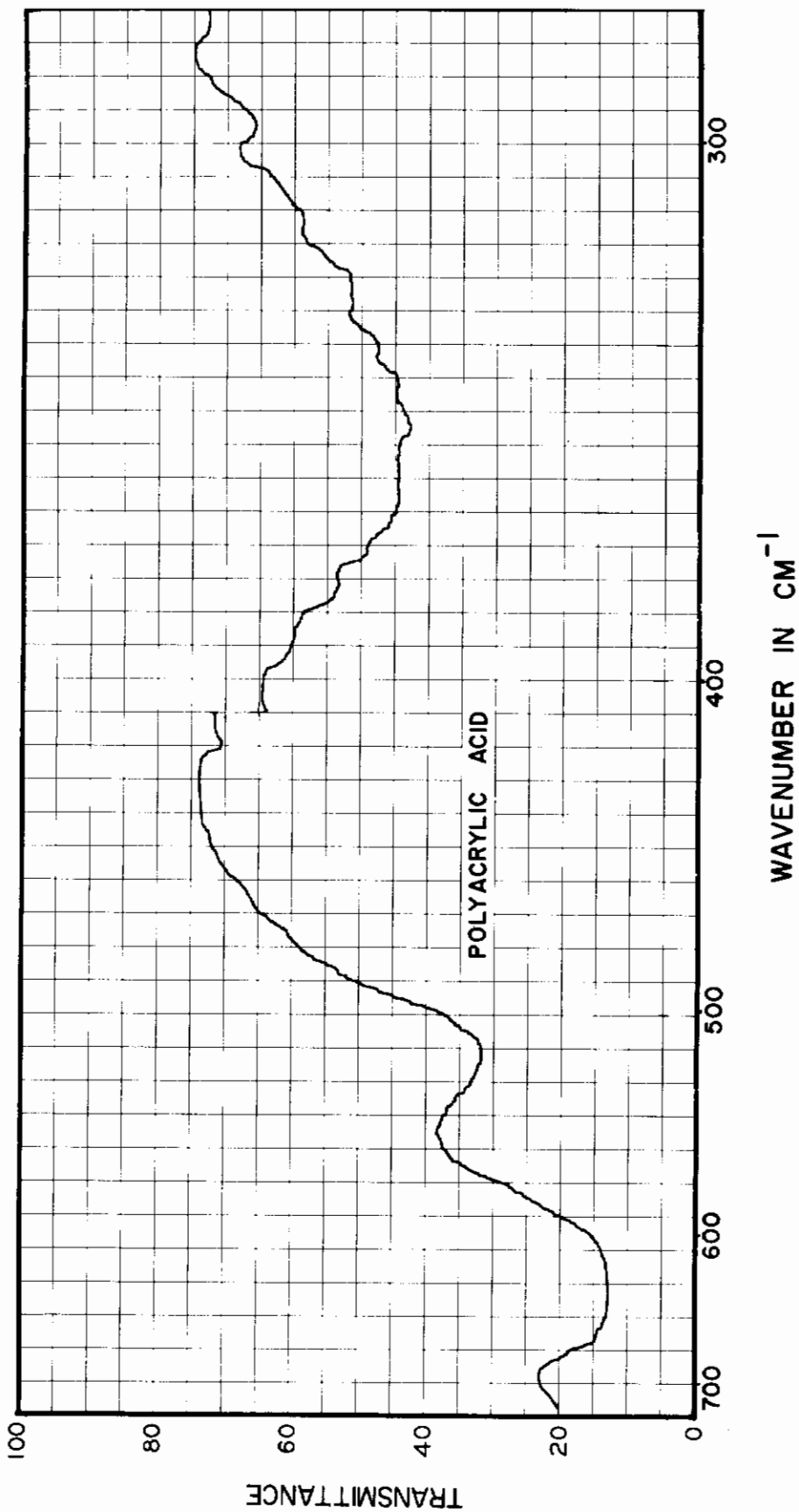


Figure 60. - Infrared Spectrum from 714 - 286 cm<sup>-1</sup> of Polyacrylic Acid  
Recorded as a film, prepared from a water solution

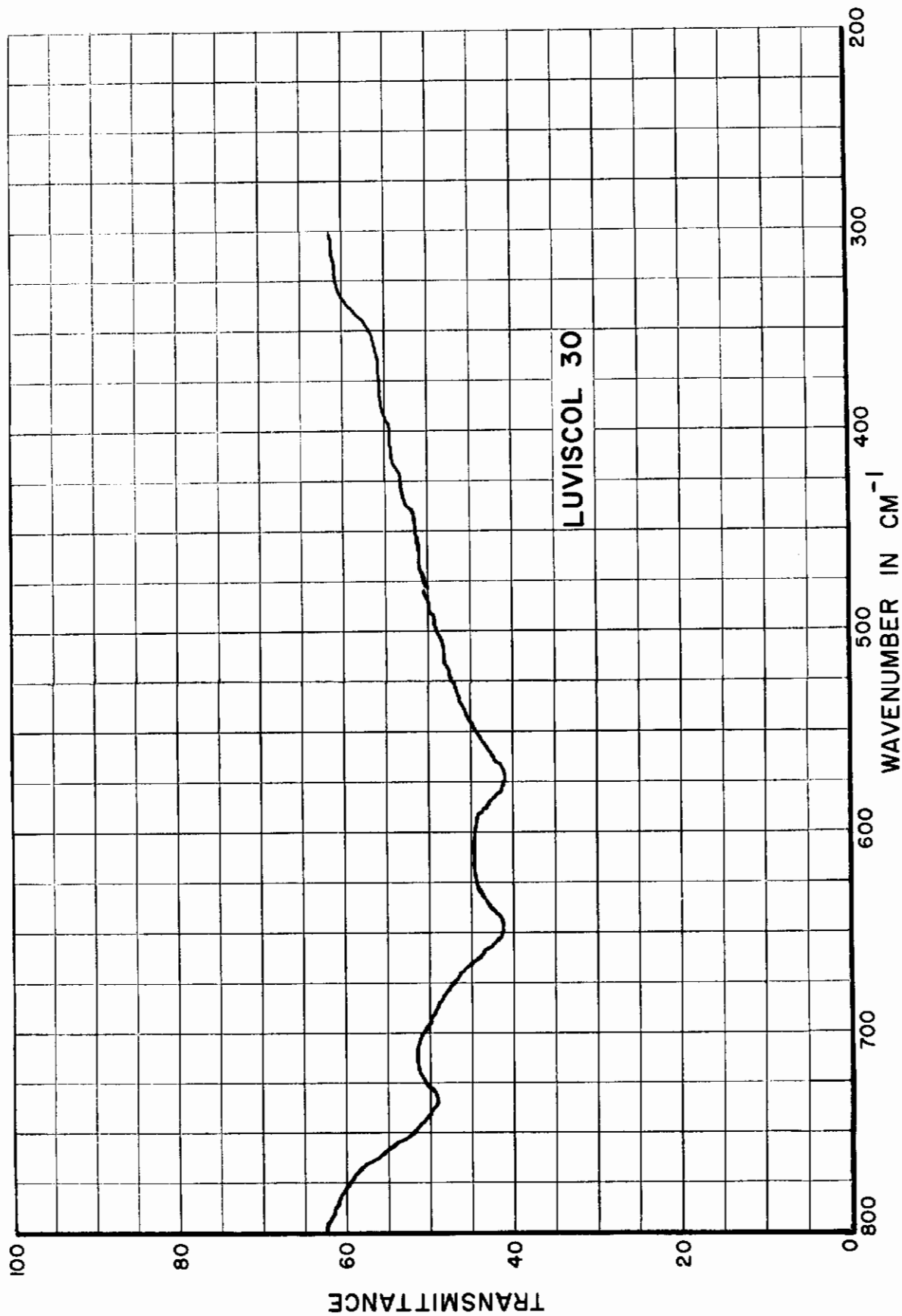


Figure 61. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Luviscol 30 (Sodium Salt of Polyacrylic Acid)  
Recorded as a KBr disk

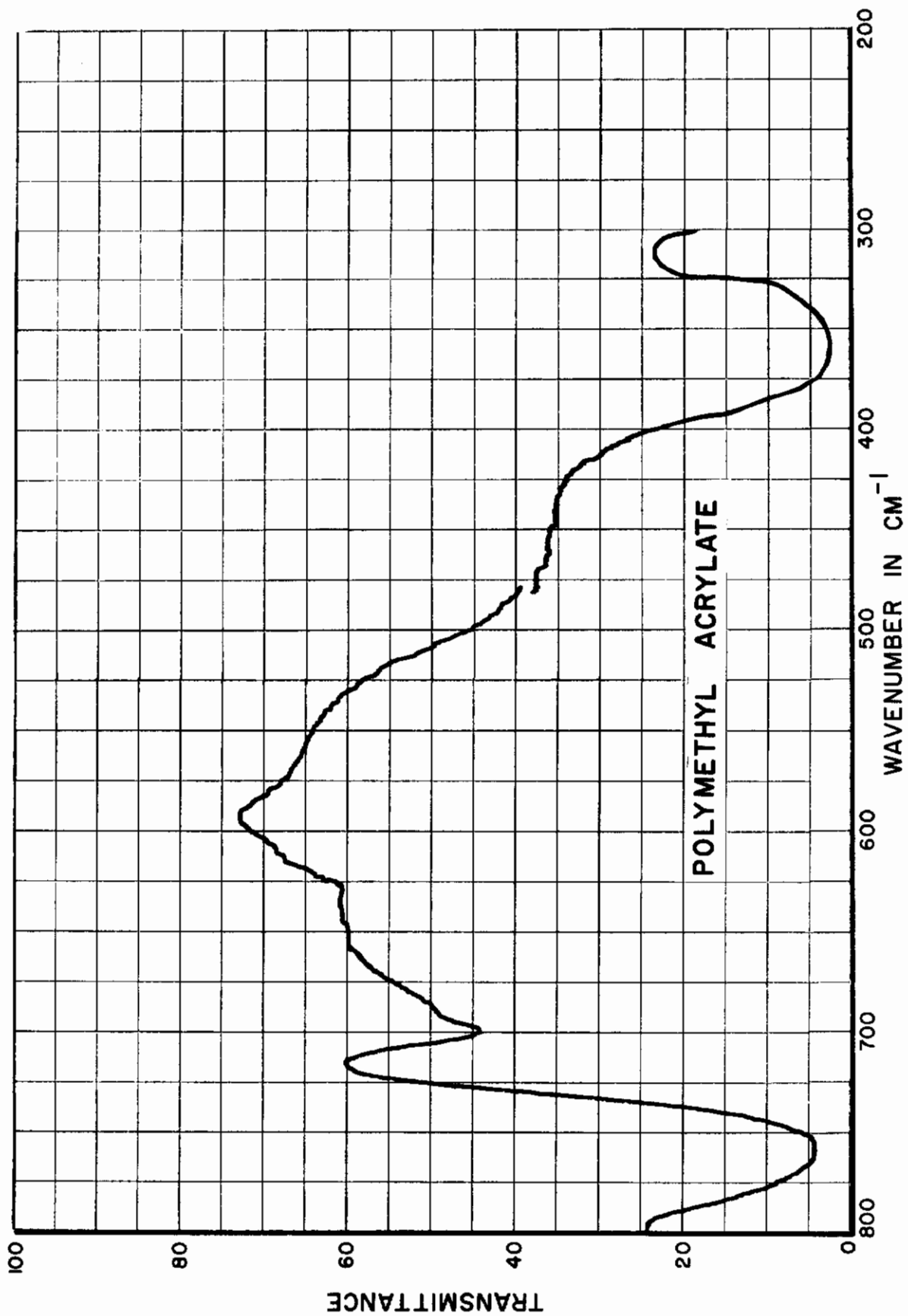


Figure 62. - Infrared Spectrum from 800 - 300  $\text{cm}^{-1}$  of Polymethylacrylate  
Recorded as a pressed film, 0.17 mm in thickness

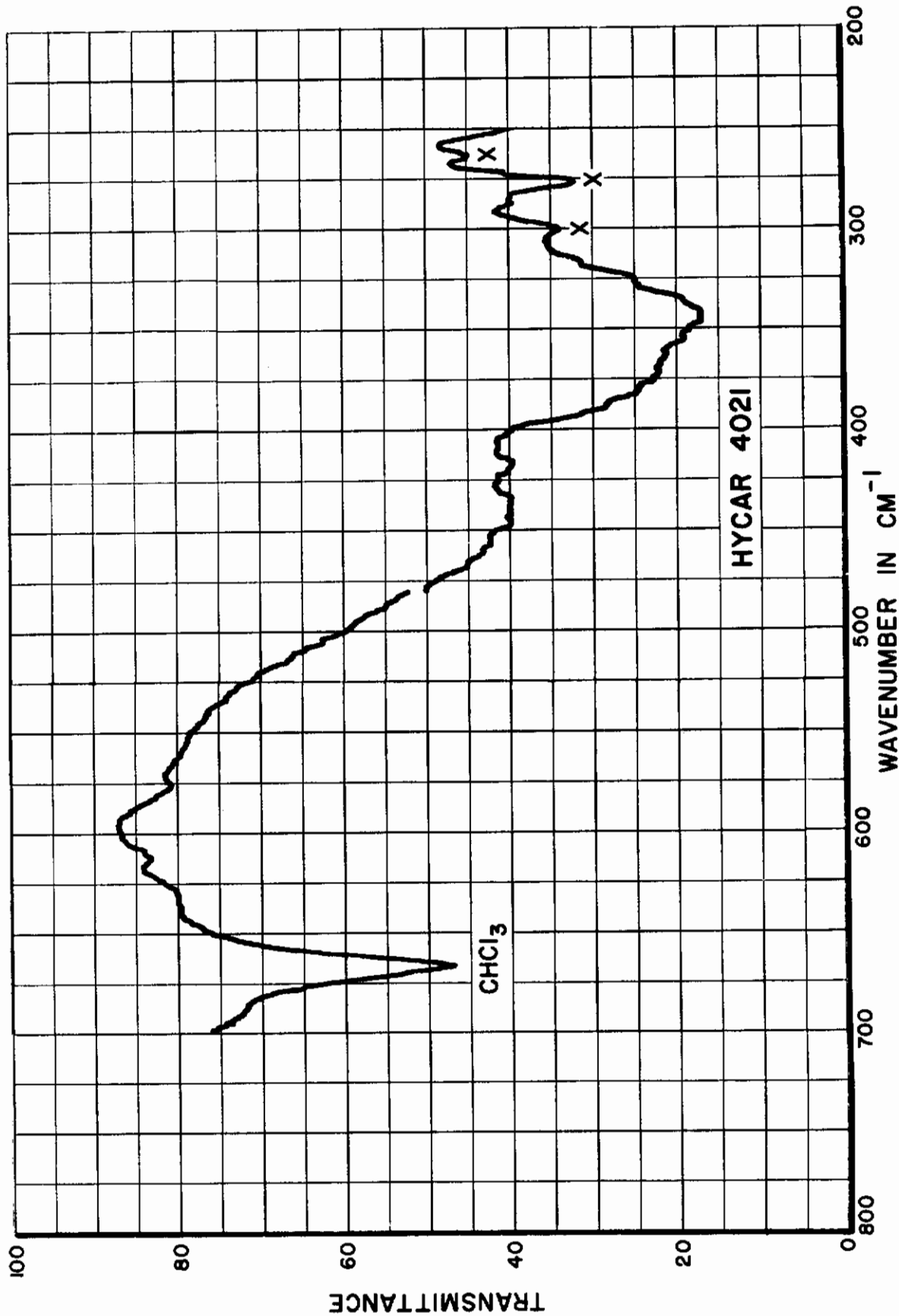


Figure 63. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Hycar 4021 (Copolymer of Ethyl Acrylate with 4% Vinyl Chloromethyl Ether) Recorded as a film approximately 0.085 mm in thickness, prepared from a chloroform solution

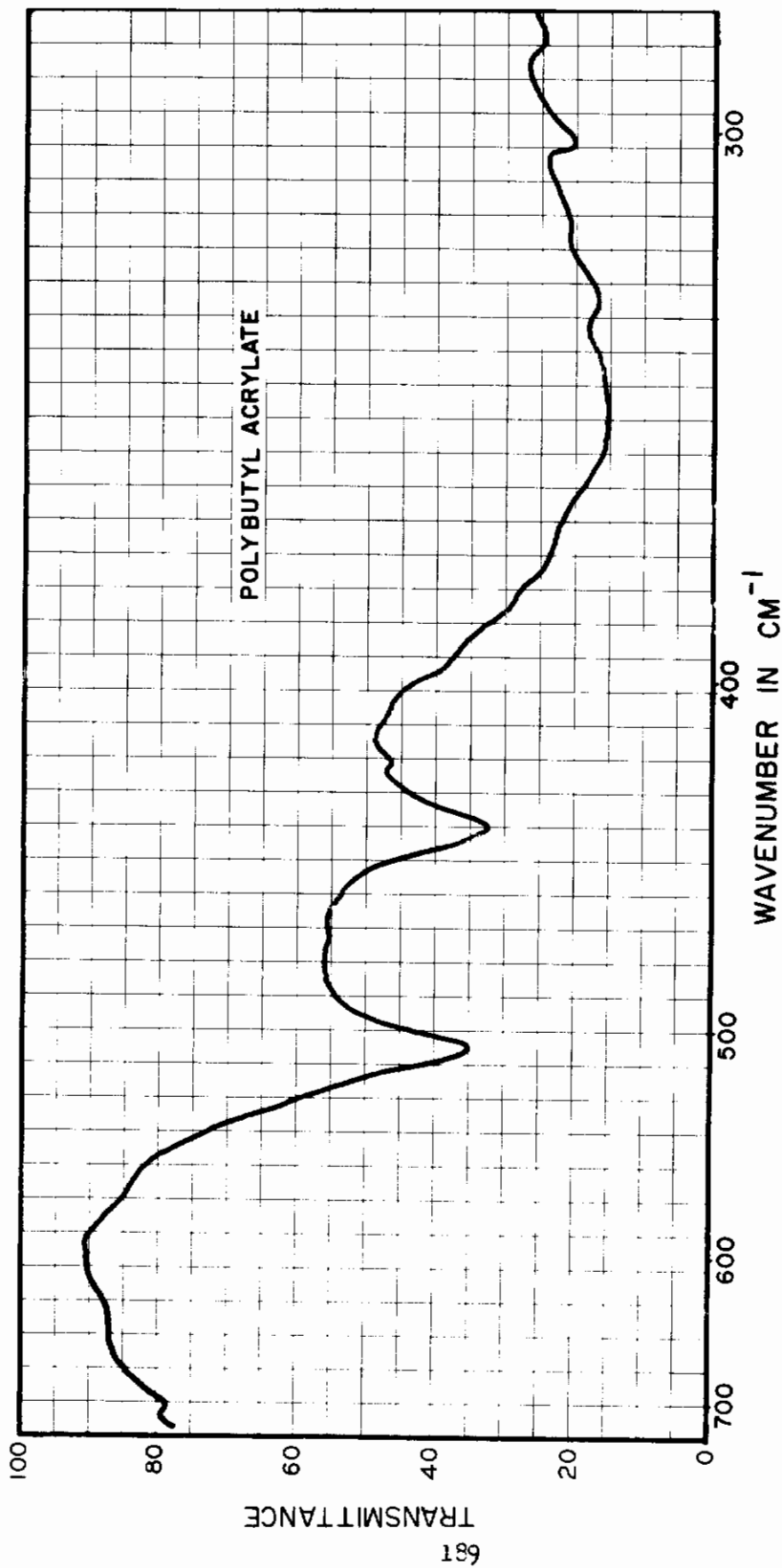


Figure 64. - Infrared Spectrum from 714 - 286 cm<sup>-1</sup> of Polybutyl Acrylate  
Recorded as a film from solution

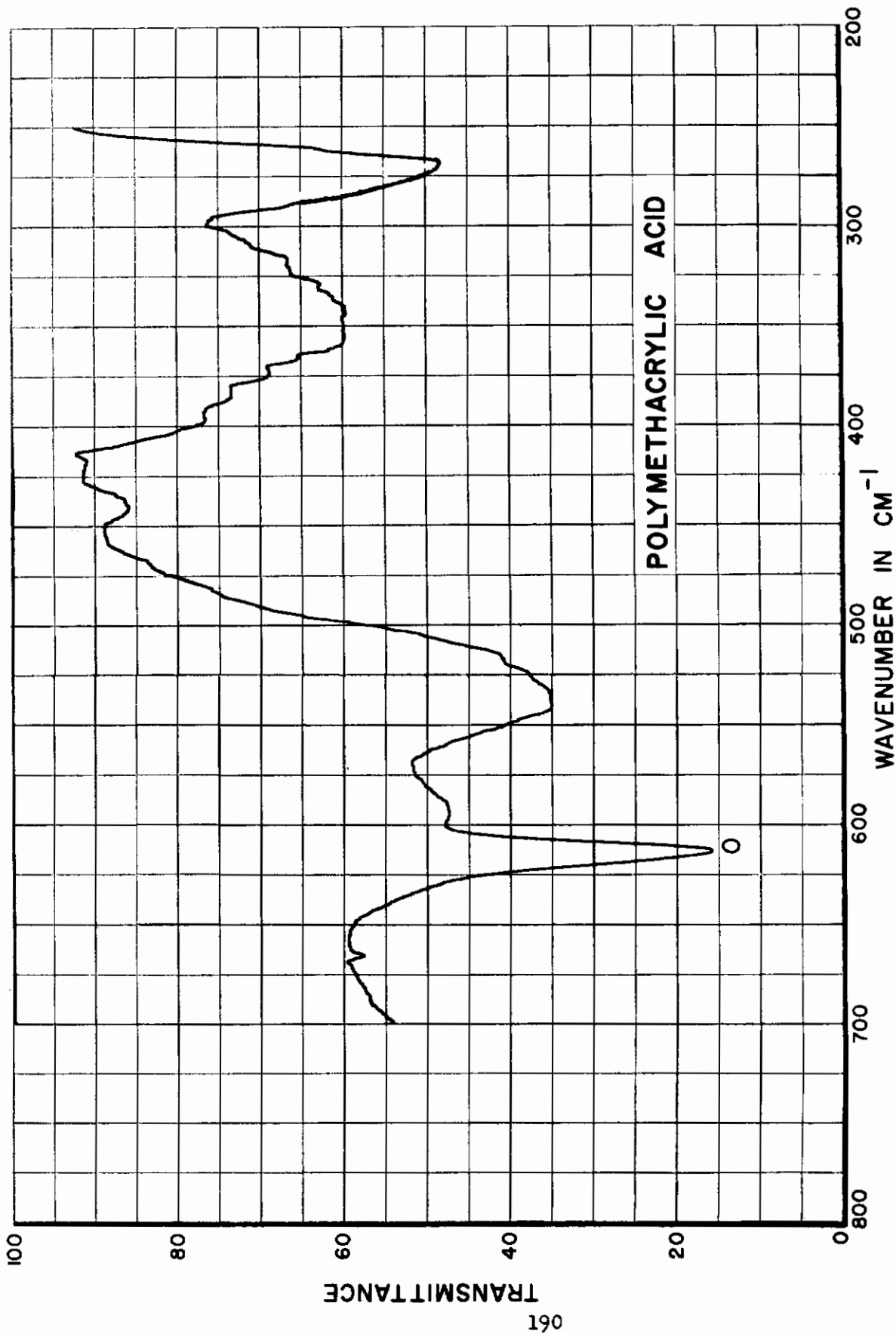


Figure 65. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Polymethacrylic Acid  
Recorded as a film, prepared from a dioxane solution.  
The band at 665 cm<sup>-1</sup> is due to atmospheric absorption.

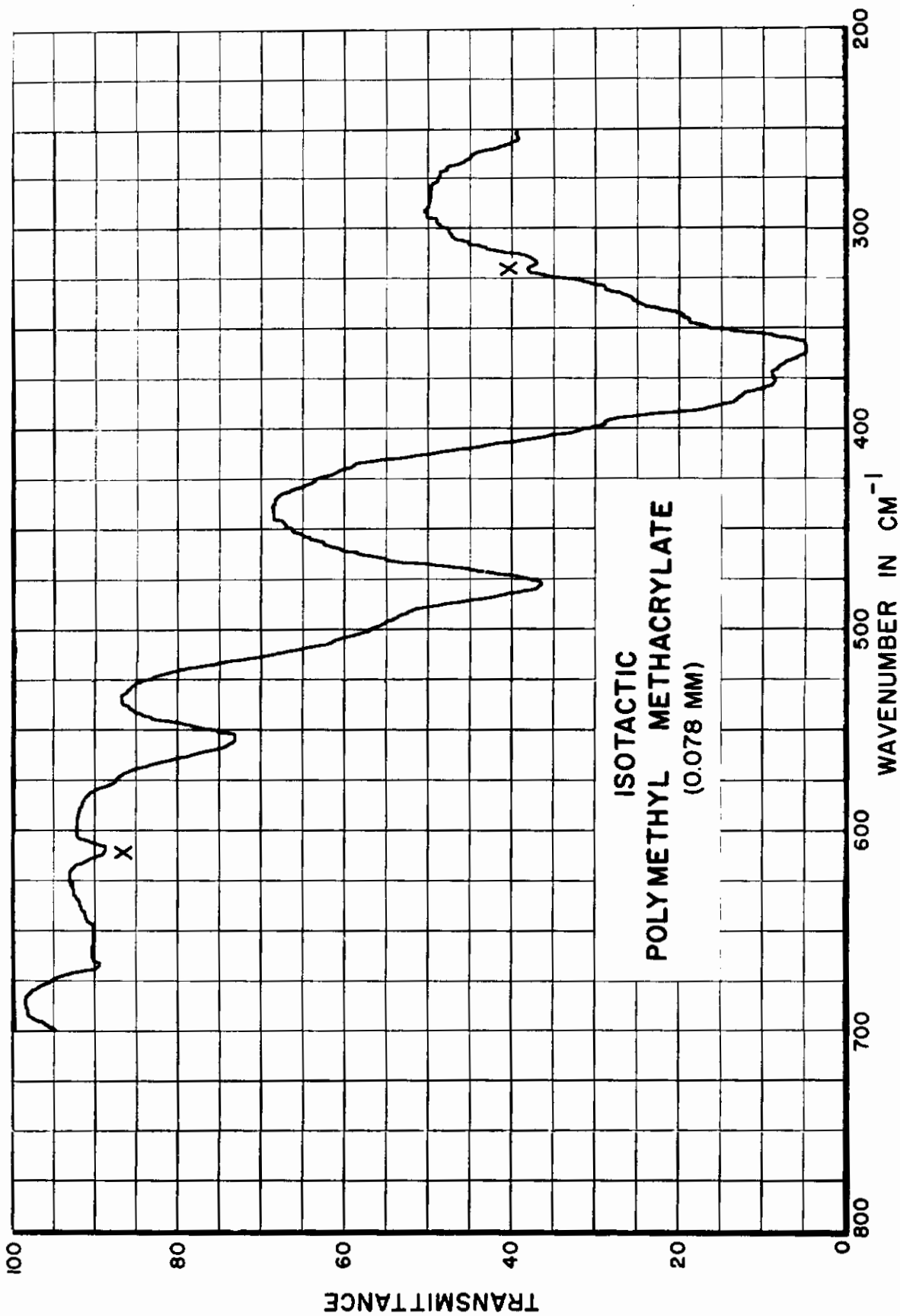


Figure 66. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of isotactic polymethyl methacrylate  
Recorded as a film, prepared from a chloroform solution  
The band at 609 cm<sup>-1</sup> is not real

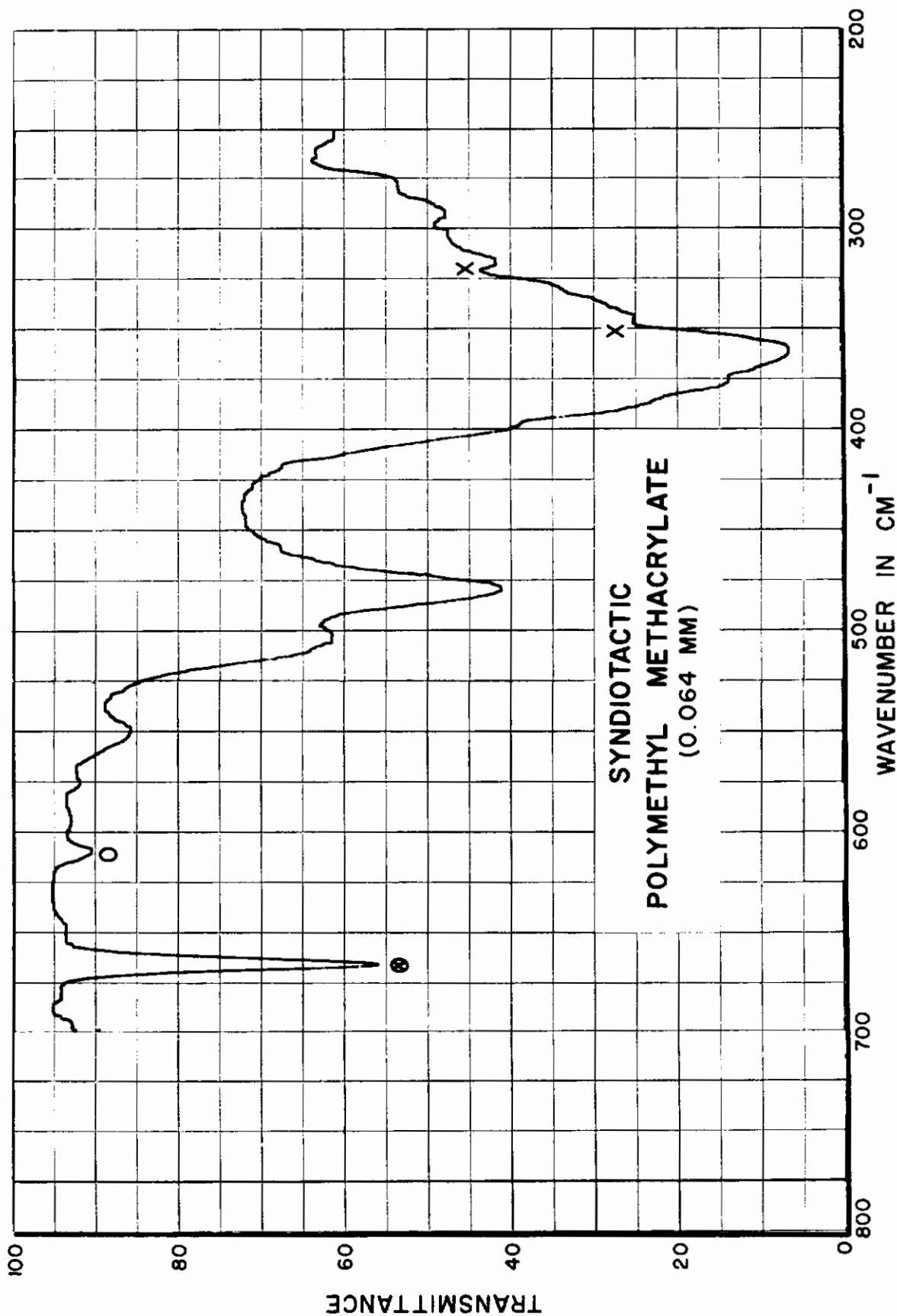


Figure 6/. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Syndiotactic Polymethyl Methacrylate  
Recorded as a film, prepared from chloroform solution  
The band at 665 cm<sup>-1</sup> is partly due to chloroform, and the one at 609 cm<sup>-1</sup>  
is not real



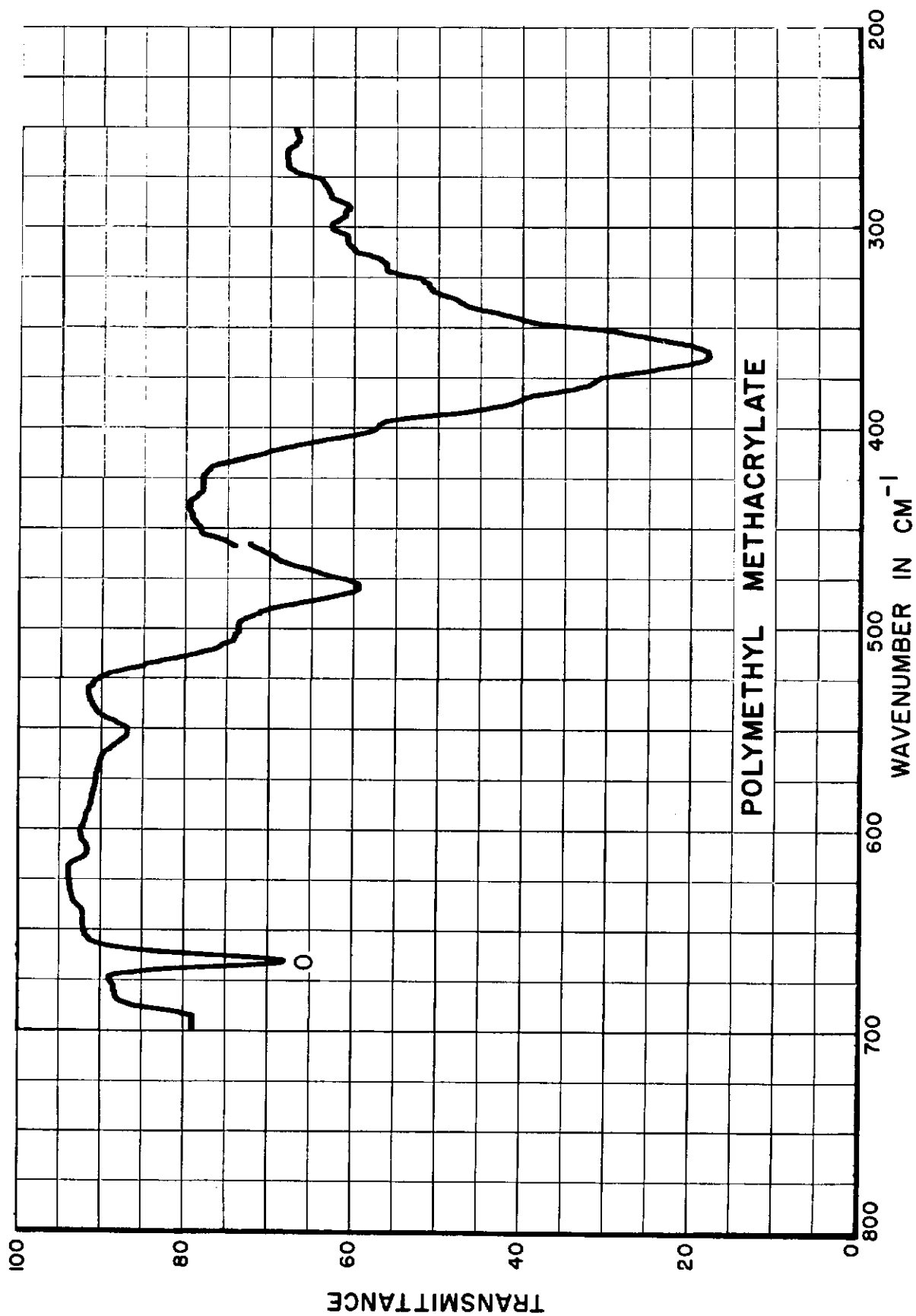


Figure 68. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Atactic Polymethyl Methacrylate  
Recorded as a film from chloroform solution  
The band at 665 cm<sup>-1</sup> is partly due to chloroform

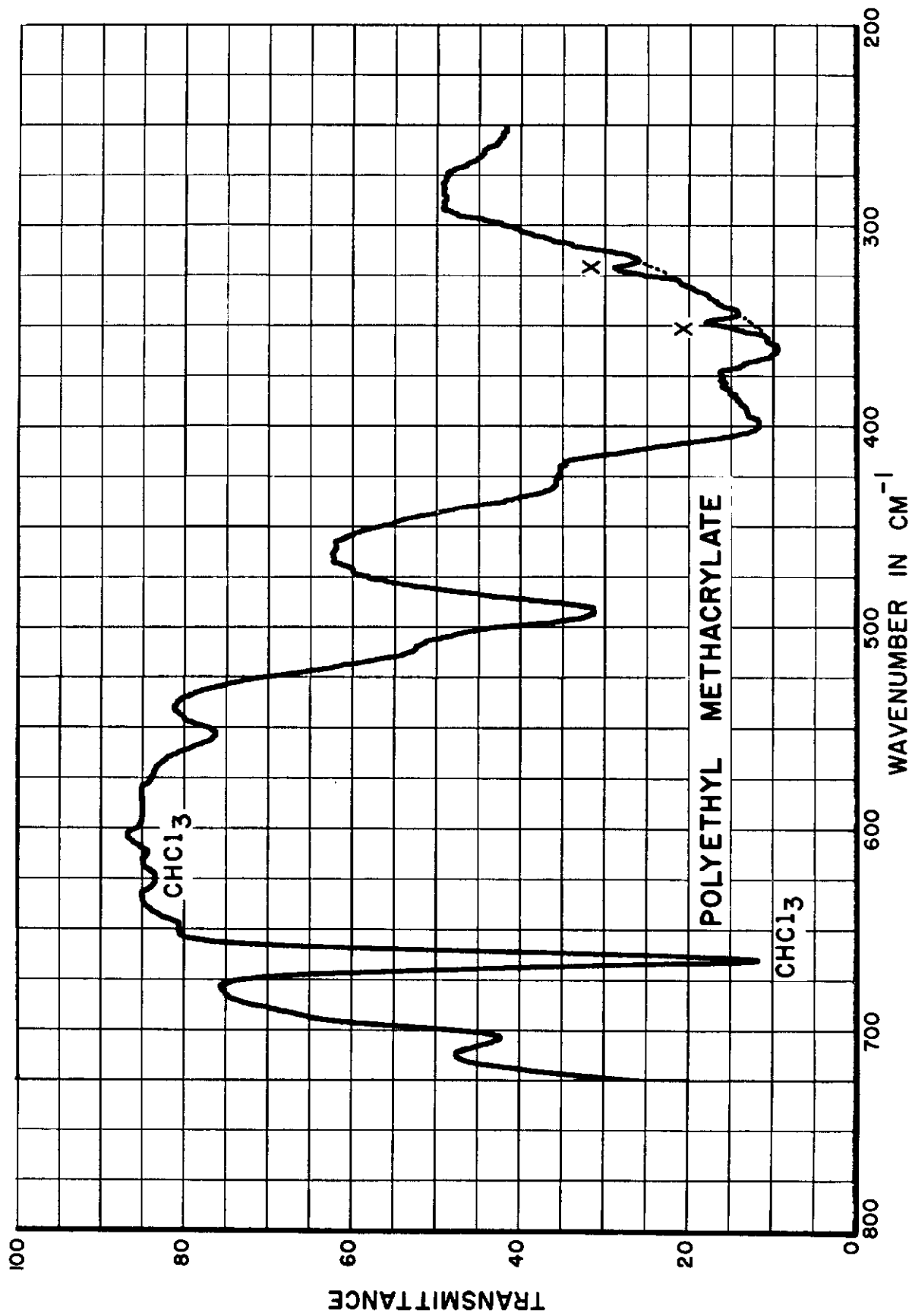


Figure 69. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Polyethyl Methacrylate  
Recorded as a film approximately 0.36 mm in thickness,  
prepared from a chloroform solution

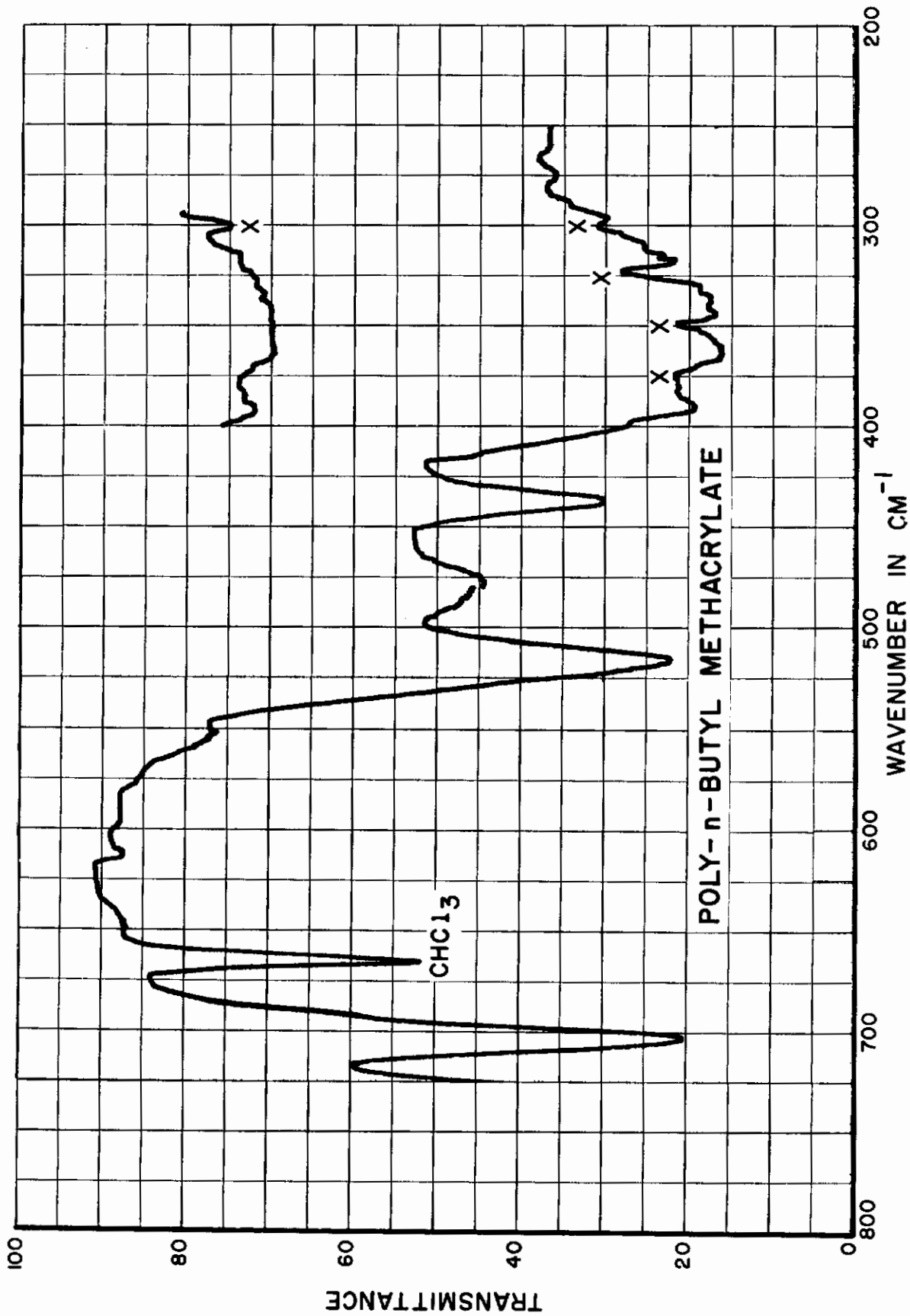


Figure 70. - Infrared Spectrum from 725 - 250  $\text{cm}^{-1}$  of Poly-n-Butyl Methacrylate  
Recorded as a film approximately 0.12 mm in thickness,  
prepared from a chloroform solution

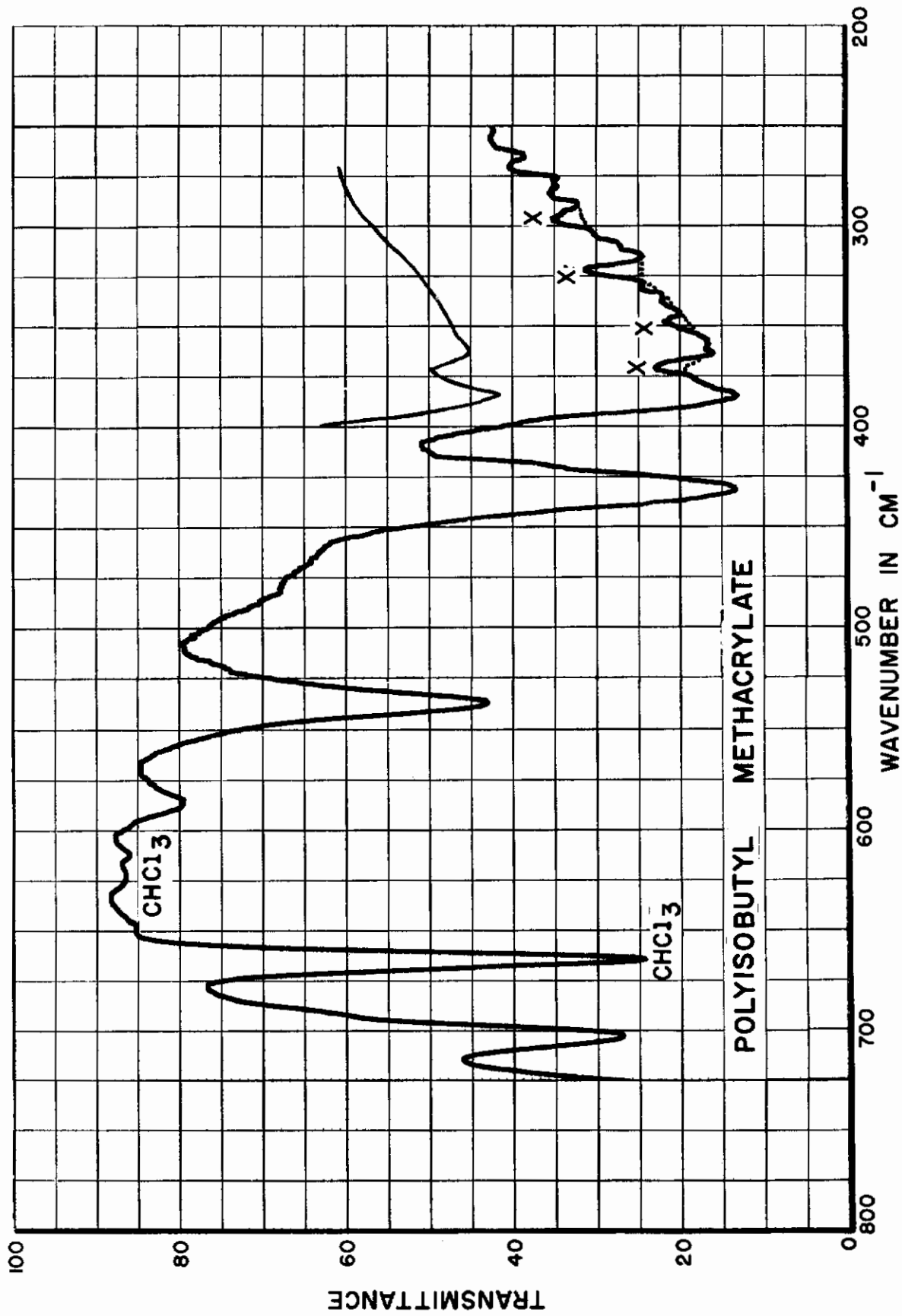


Figure 71. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Polyisobutyl Methacrylate  
Recorded as a film, prepared from a chloroform solution

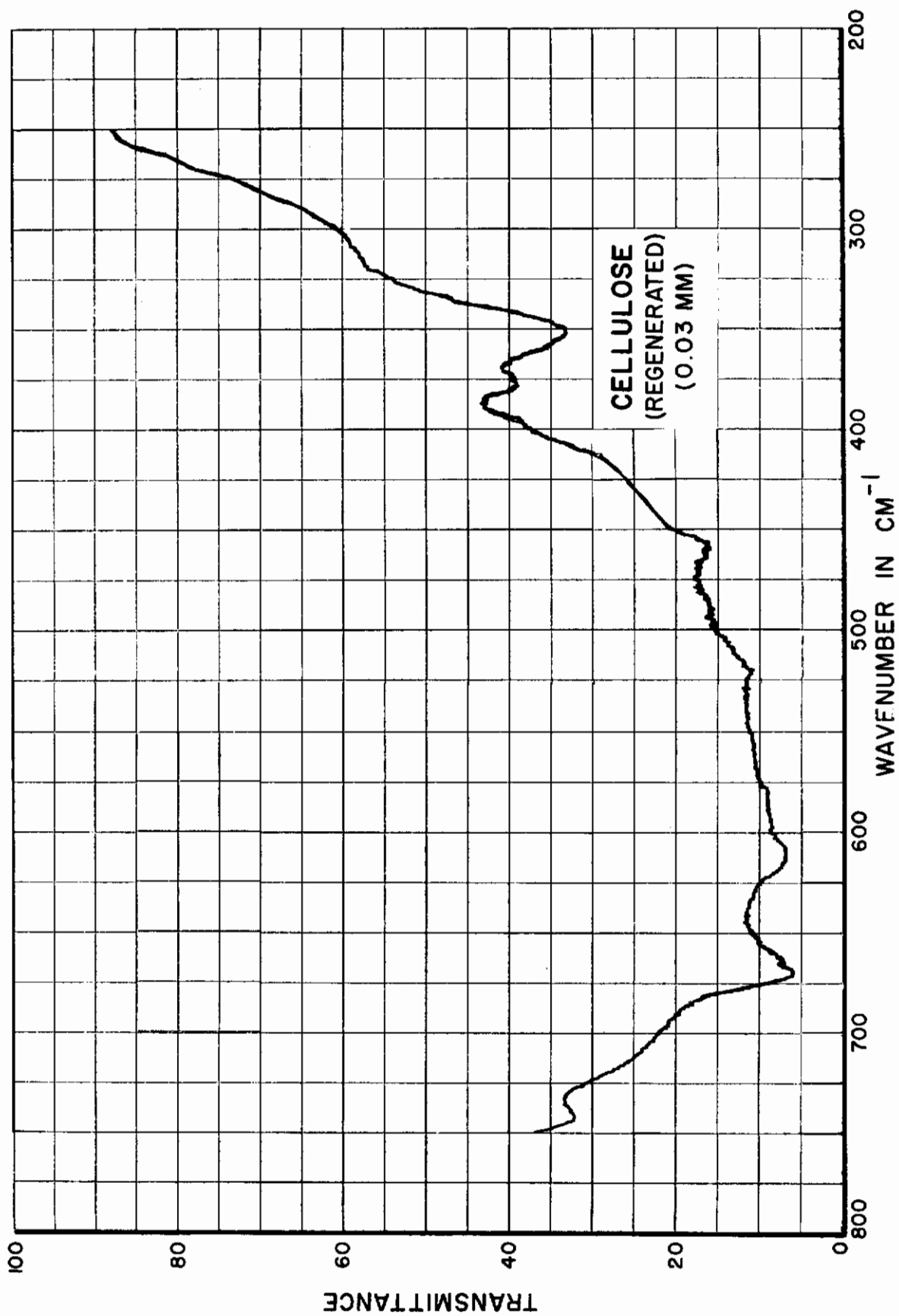


Figure 72. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Regenerated Cellulose (Cellophane)  
Recorded as a film 0.03 mm in thickness

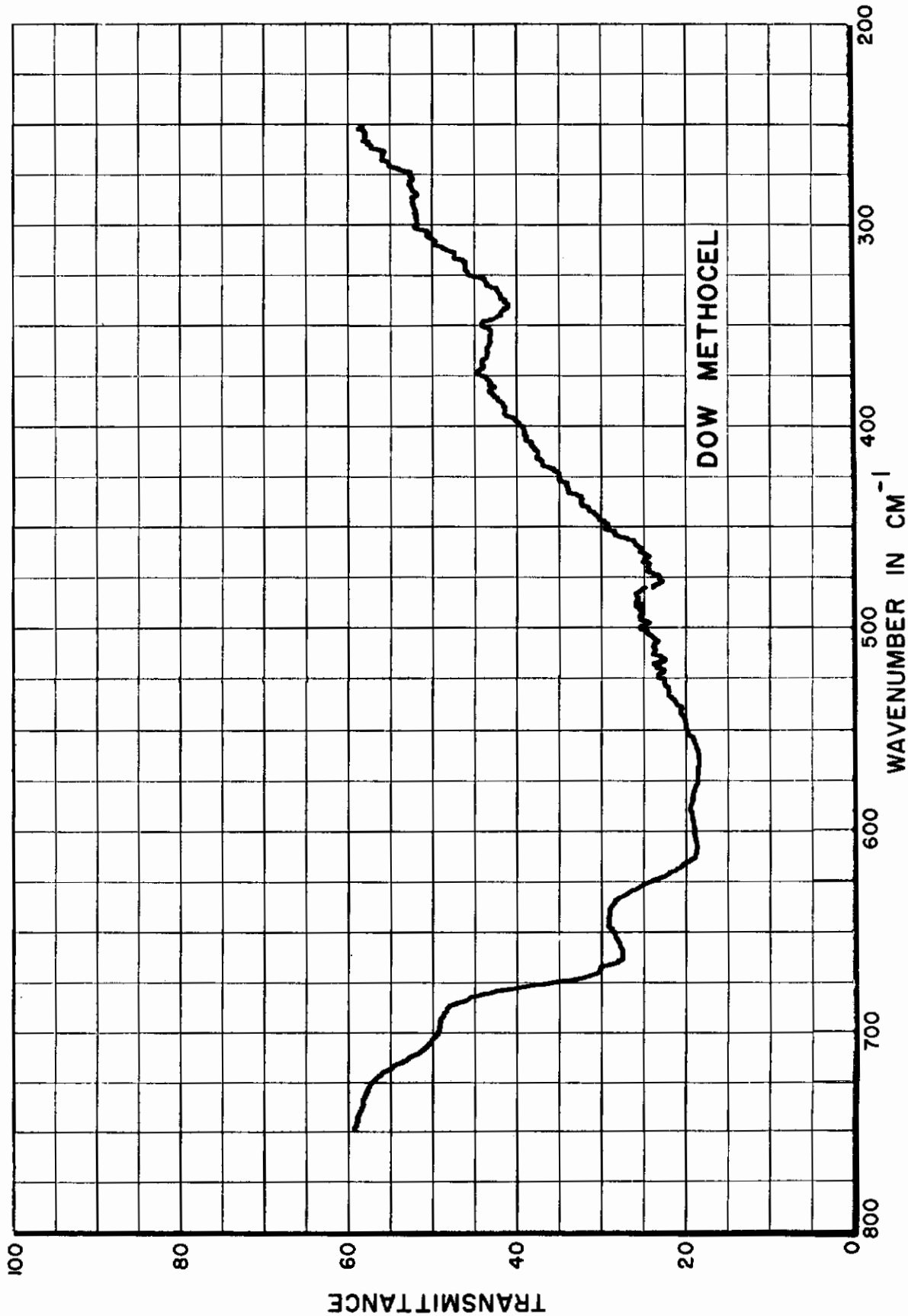


Figure 73. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Dow Methocel (Methyl Cellulose) Recorded as a film approximately 0.03 mm in thickness, prepared from a water solution.

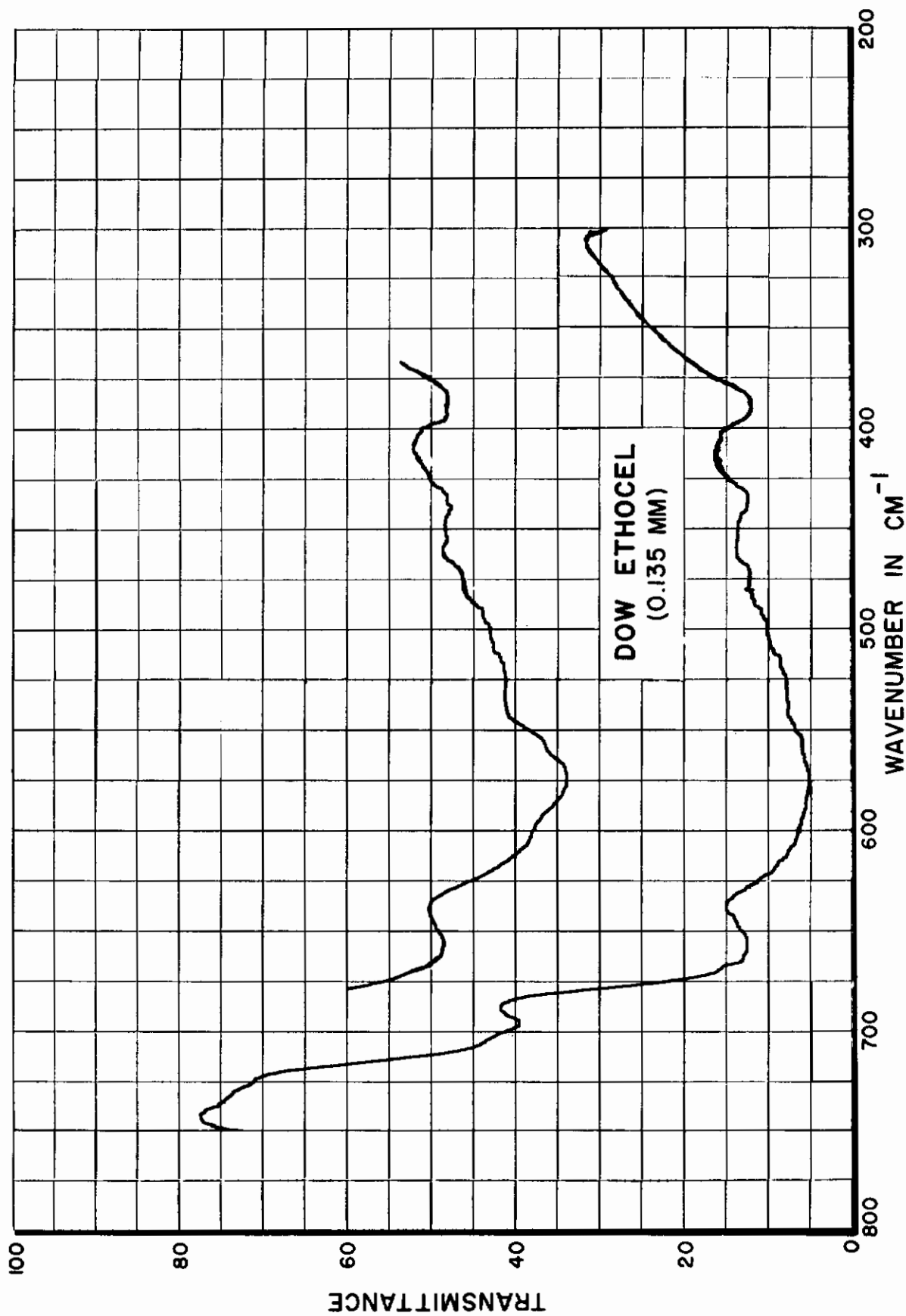


Figure 74. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Dow Ethocel (Ethyl Cellulose)  
Recorded as a film 0.135 mm in thickness

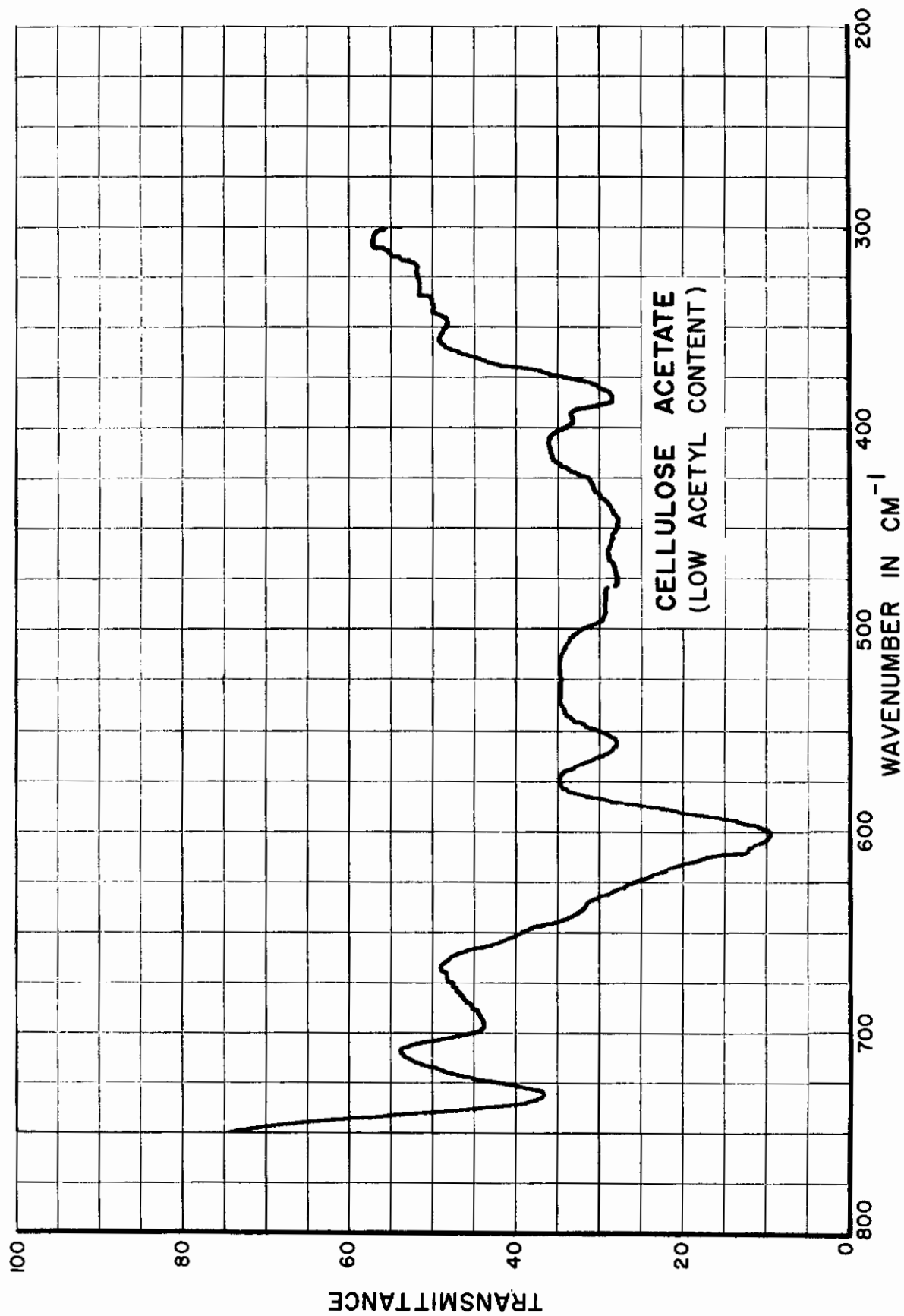


Figure 75. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Cellulose Acetate (Low Acetyl Content) Recorded as a film approximately 0.07 mm in thickness, prepared from a methylene chloride-methanol solution (9:1)



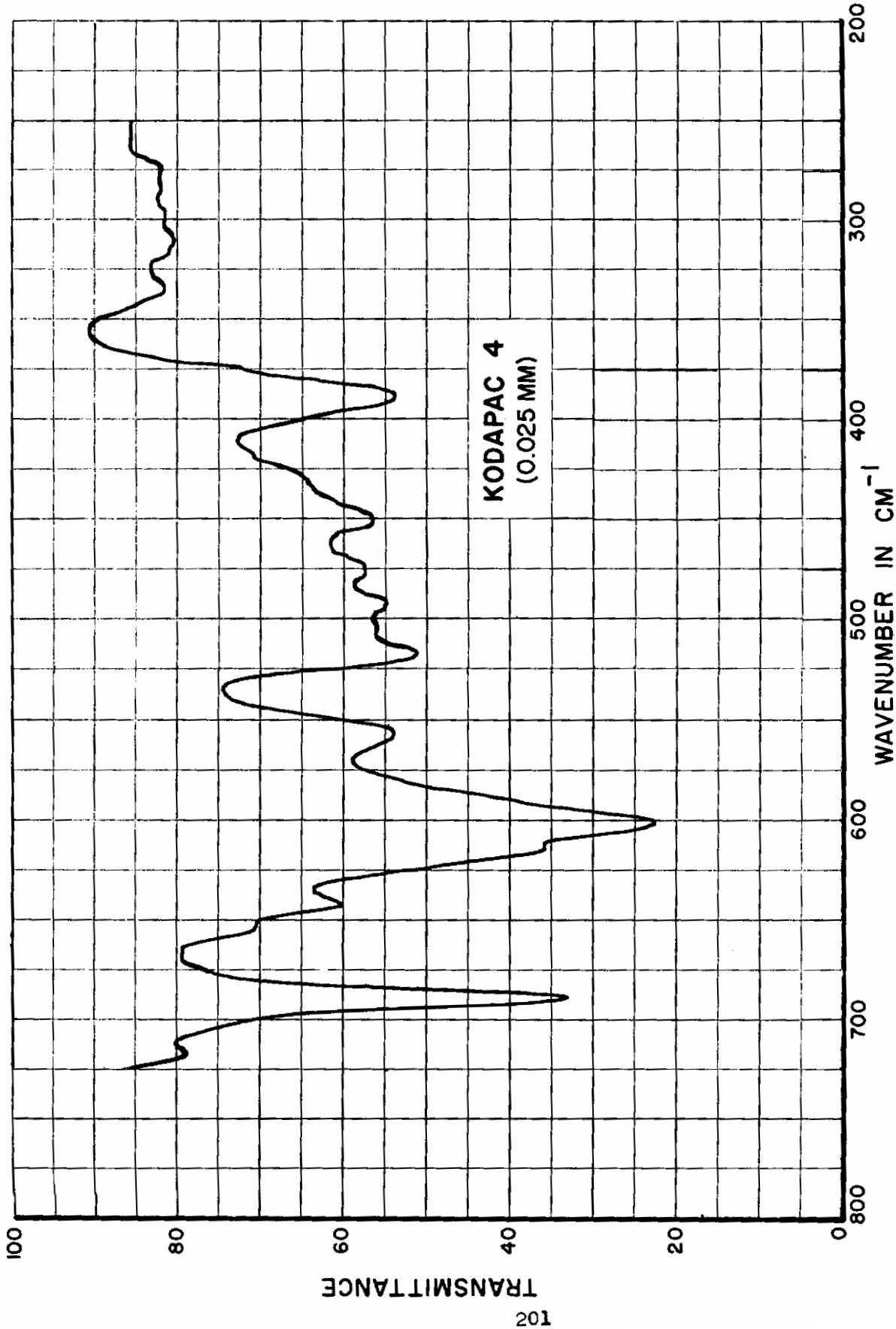


Figure 76. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Kodapac 4 (Cellulose Triacetate) Recorded as a film 0.025 mm in thickness

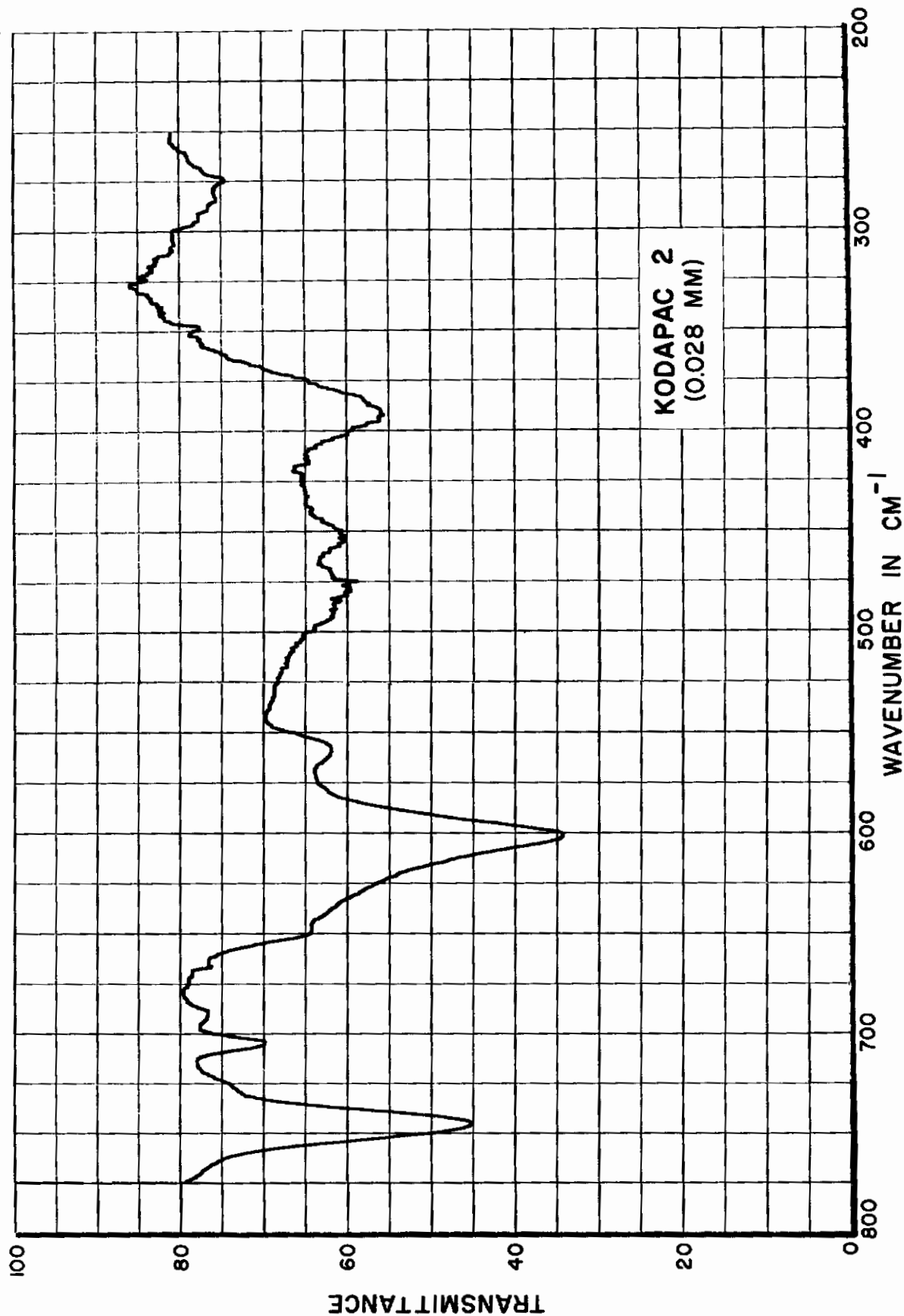


Figure 77. - Infrared Spectrum from 775 - 250 cm<sup>-1</sup> of Kodapac 2  
Recorded as a film 0.028 mm in thickness

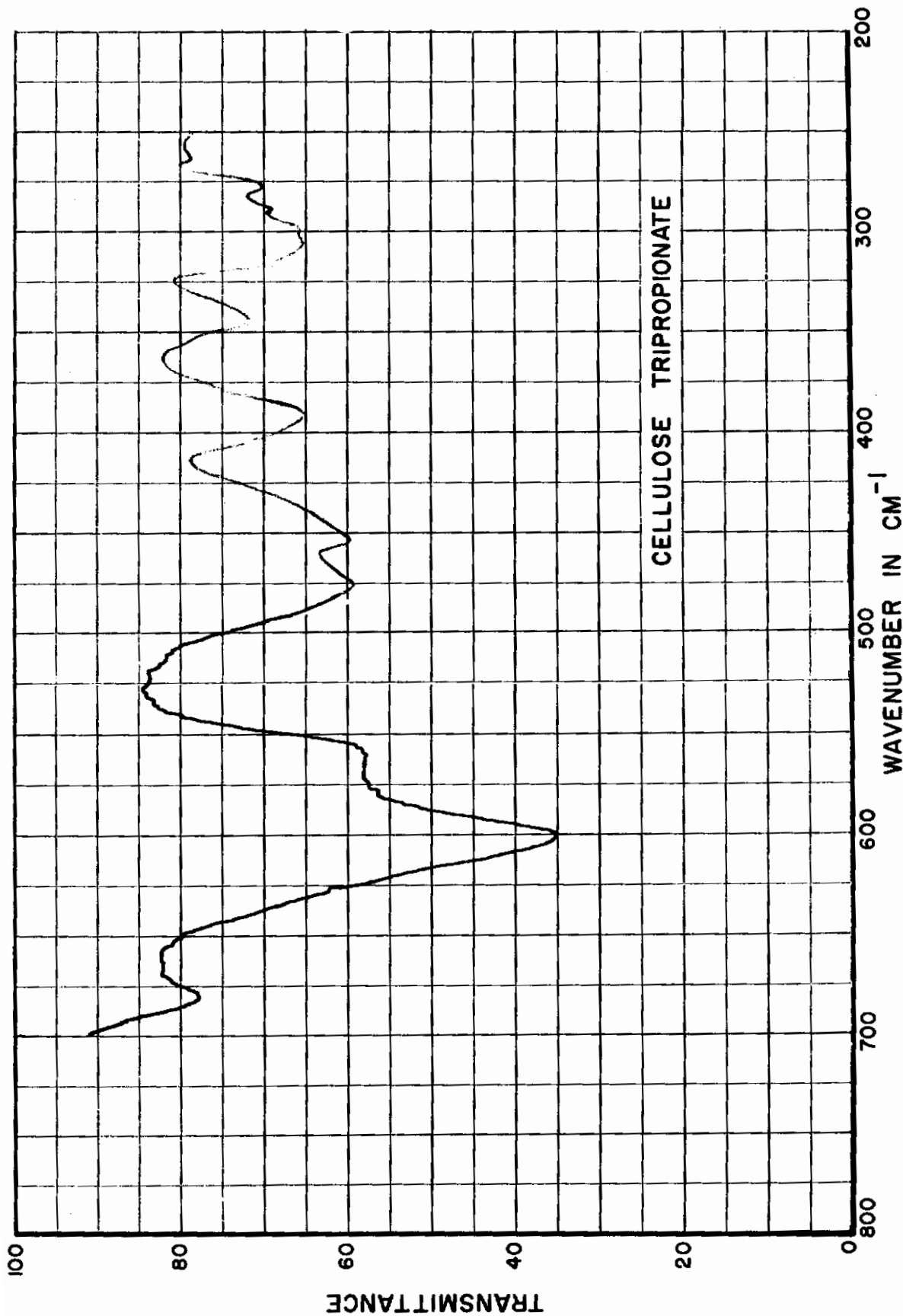


Figure 78. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Cellulose Tripropionate  
Recorded as a film, prepared from benzene solution

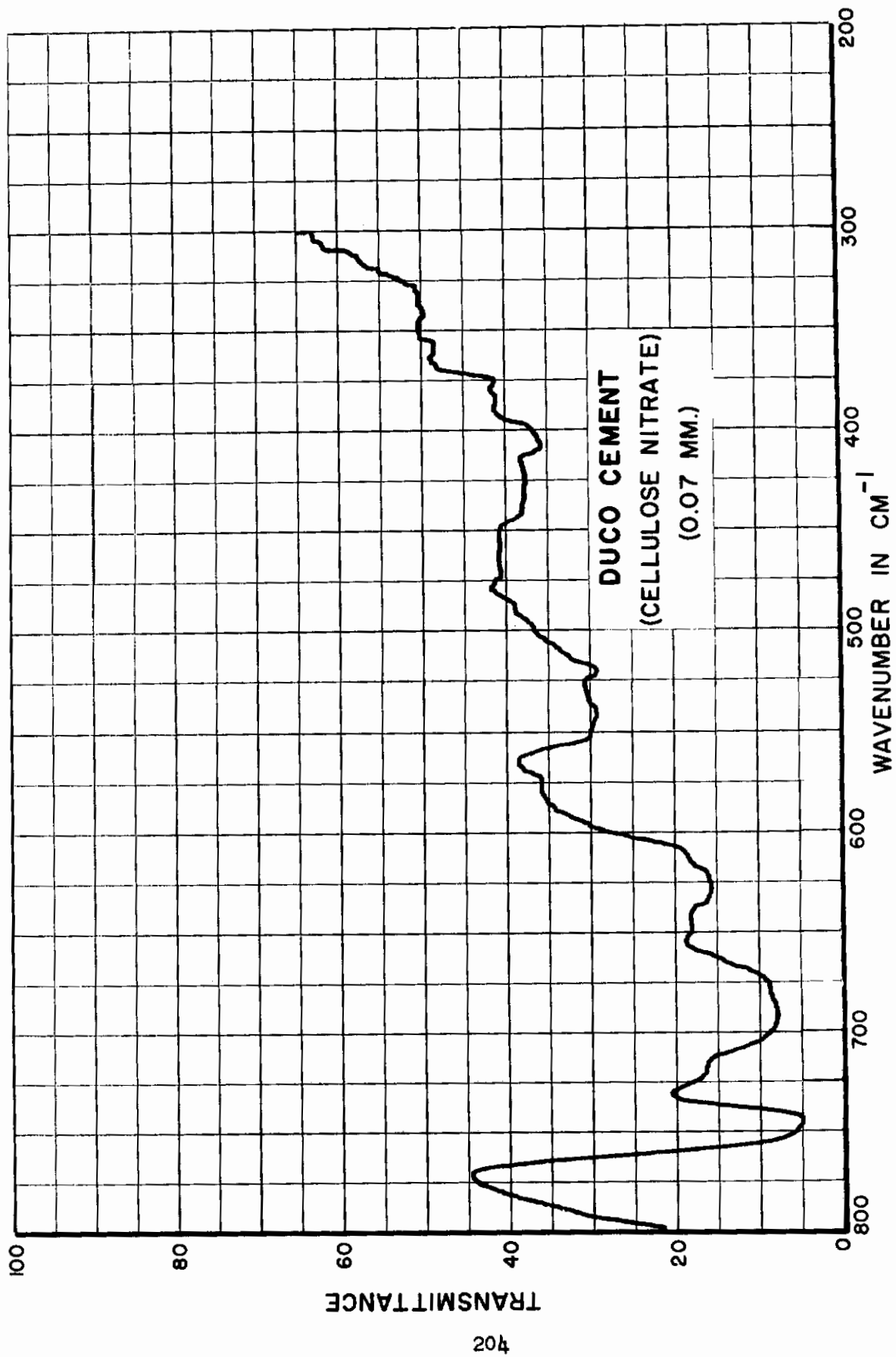


Figure 79. - Infrared Spectrum from 800 - 300  $\text{cm}^{-1}$  of Duco Cement (Cellulose Nitrate)  
Recorded as a film

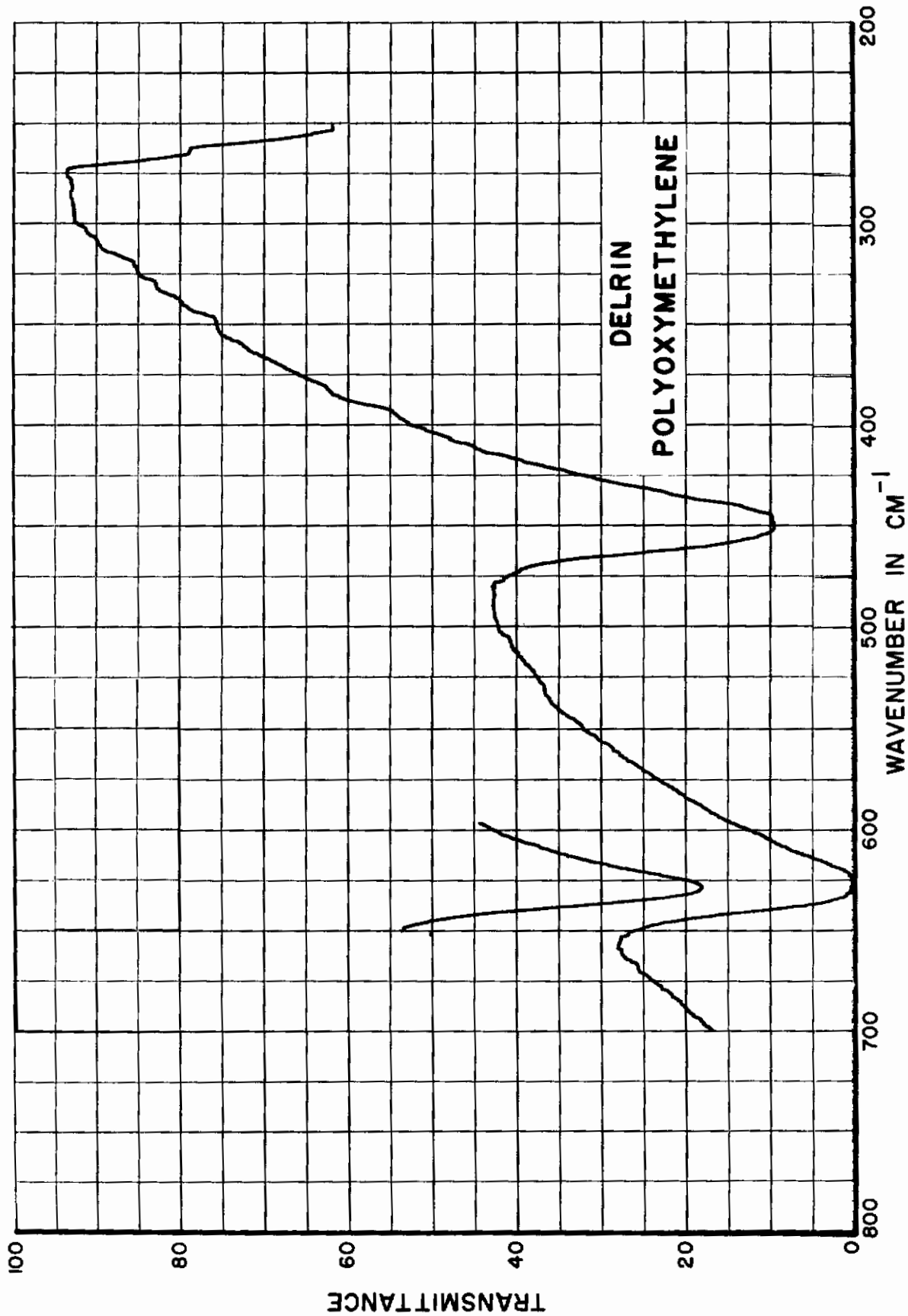


Figure 80. - Infrared Spectrum from 700 - 250  $\text{cm}^{-1}$  of Delrin (Polyoxymethylene)  
Recorded as a KBr disk

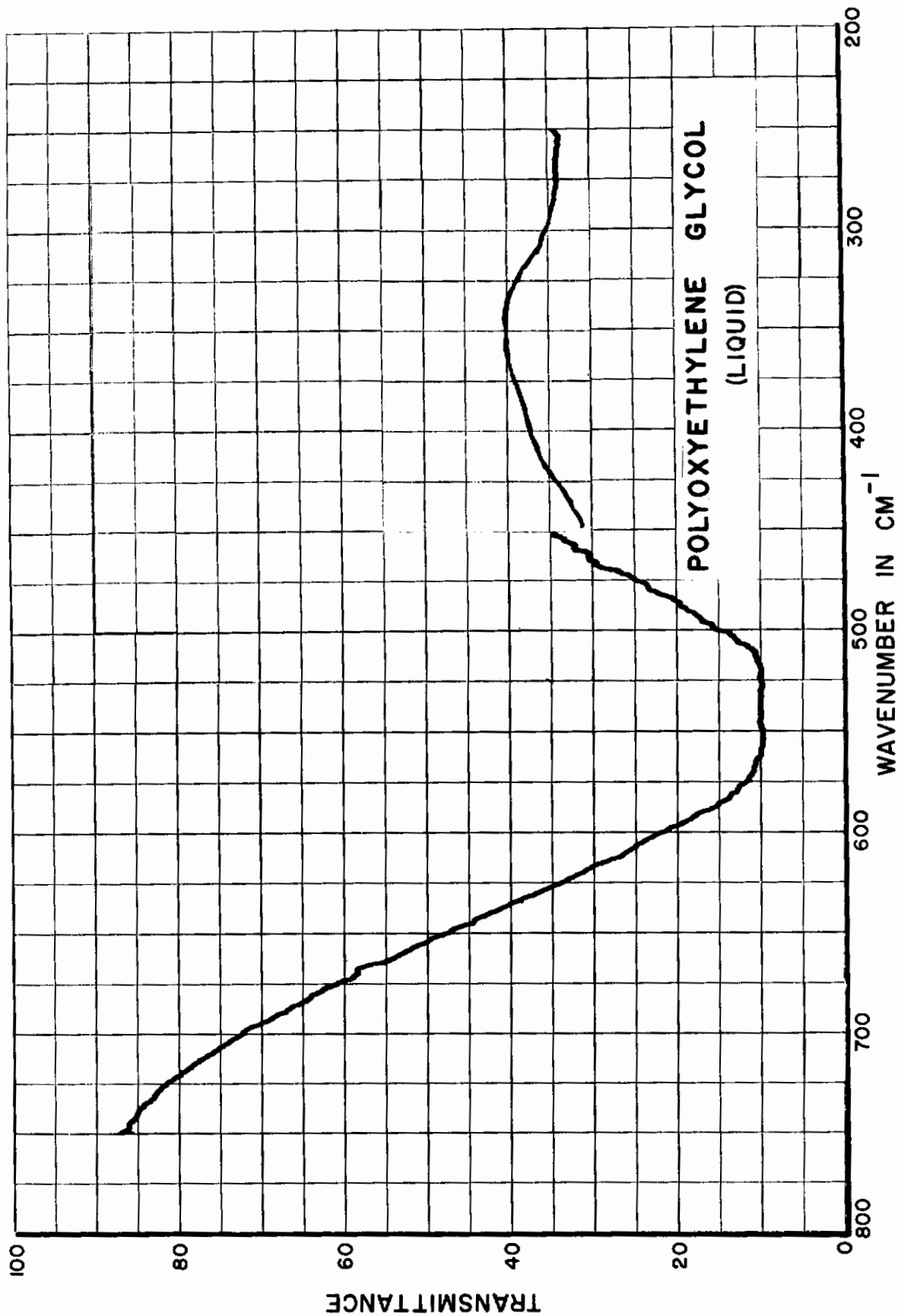


Figure 81. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Polyoxyethylene Glycol (Liquid)  
Recorded as a film

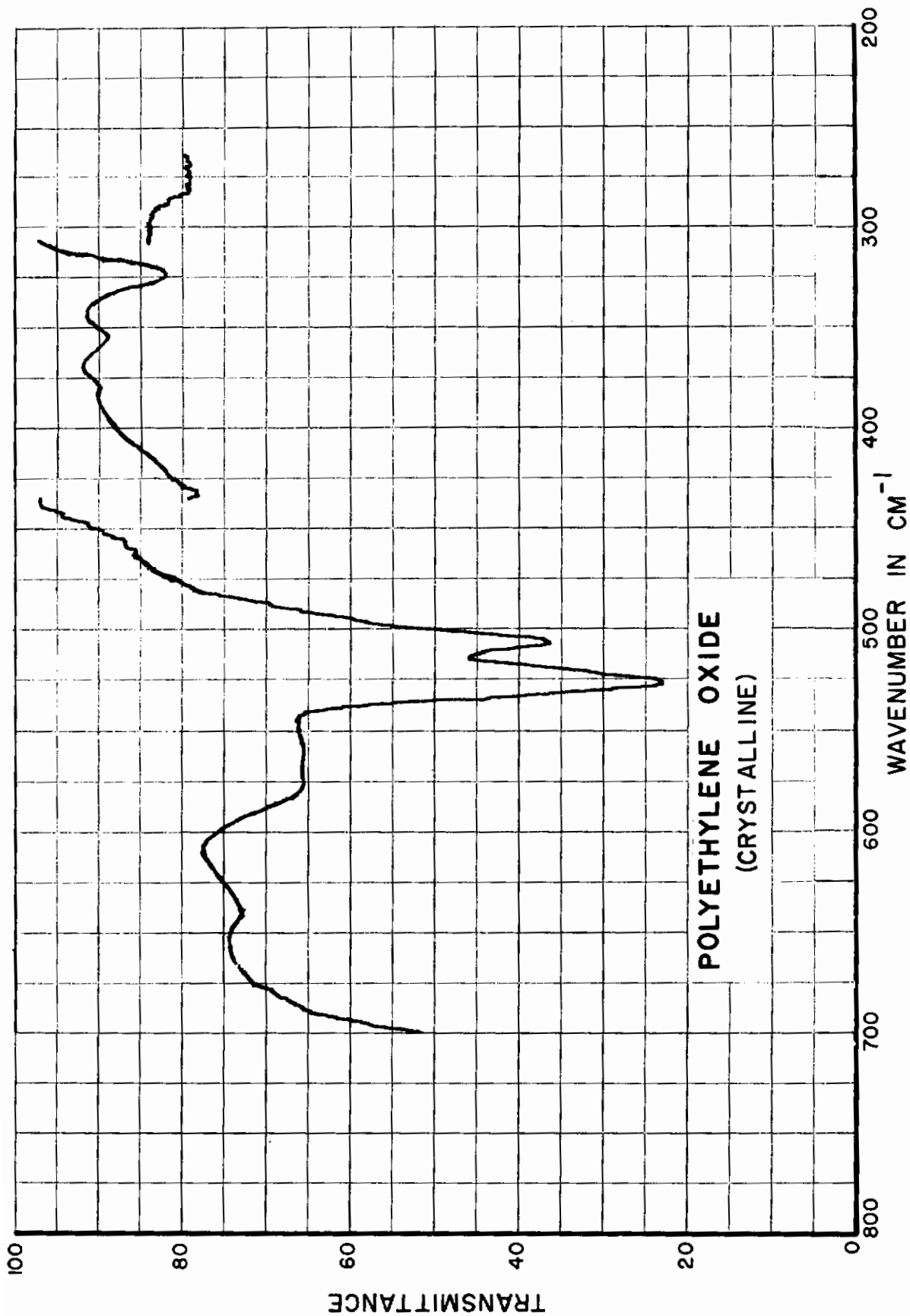


Figure 62. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Polyethylene Oxide (Crystalline)  
Recorded as a Nujol mull

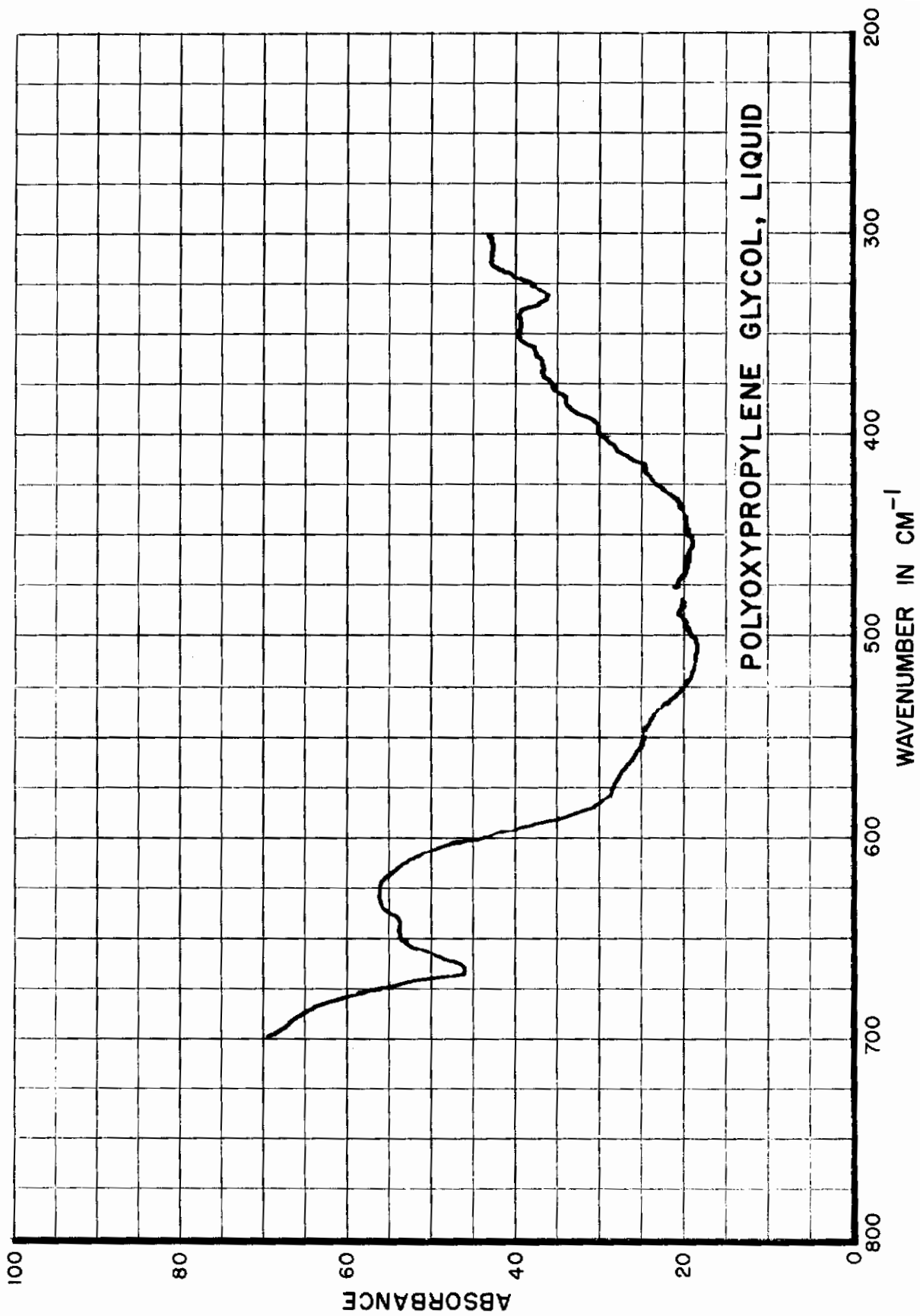


Figure 33. - Infrared Spectrum from 700 - 300  $\text{cm}^{-1}$  of Polyoxypropylene Glycol (Liquid)  
Recorded in a 0.092 mm CsBr cell



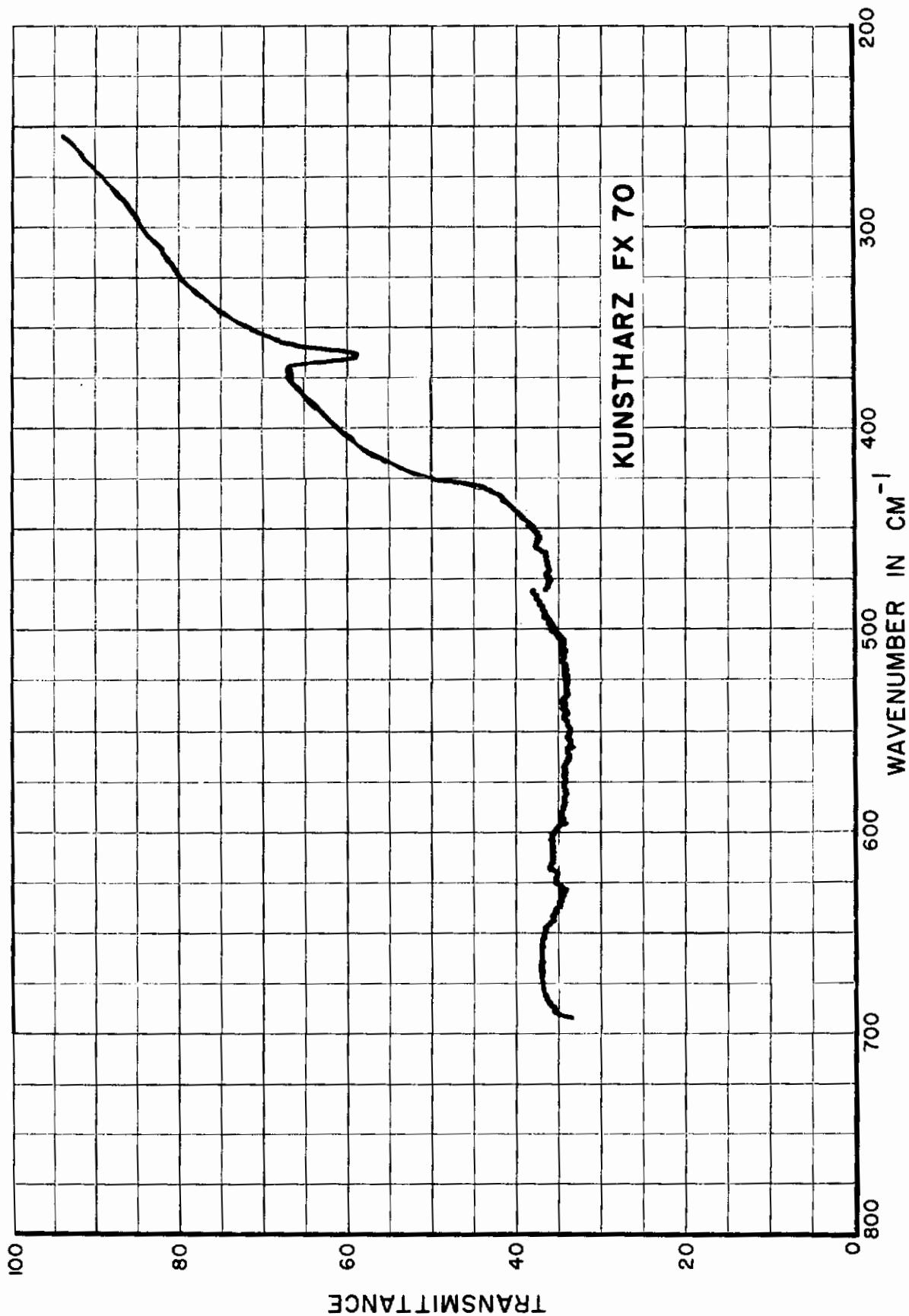


Figure 84. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Kunstharz FX 70 (Acetaldehyde Resin) Recorded as a film, prepared from a chloroform solution

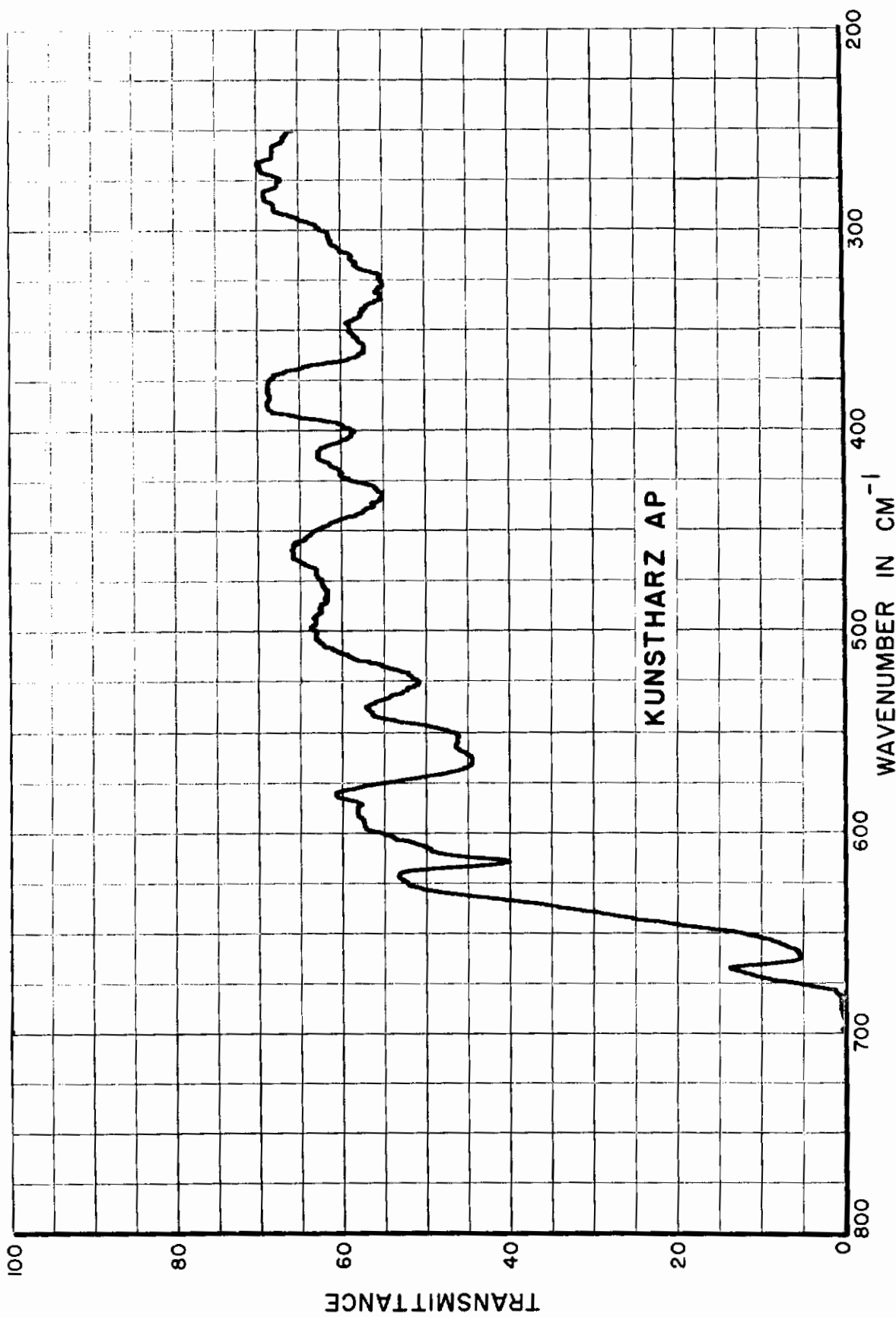
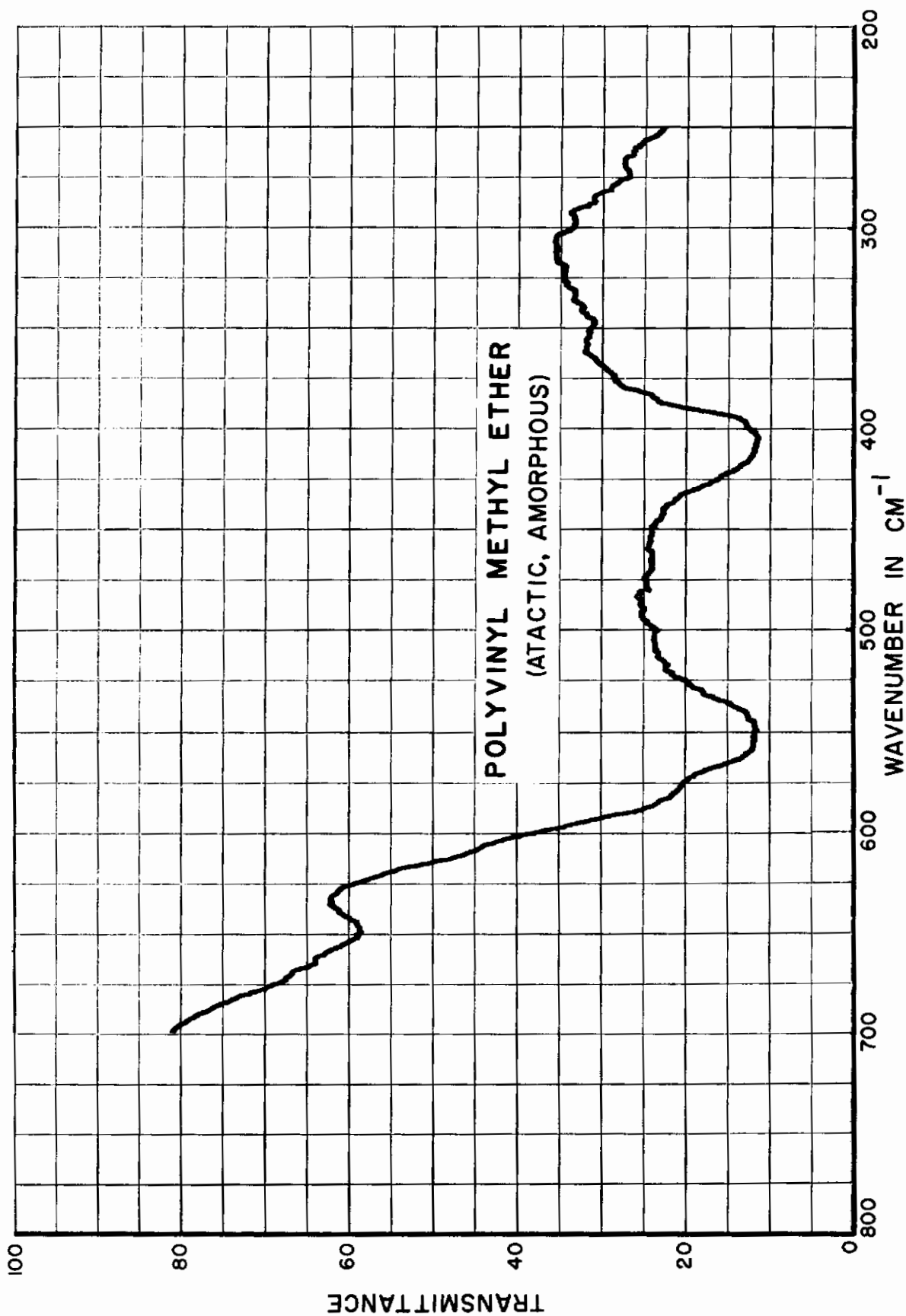


Figure 35. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Kunstharz AP (Acetophenone-Formaldehyde Resin),

Recorded as a film, prepared from chloroform solution



POLYVINYL METHYL ETHER  
(ATACTIC, AMORPHOUS)

Figure 86. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Polyvinyl Methyl Ether (Atactic, Amorphous)  
Recorded as a film from solution

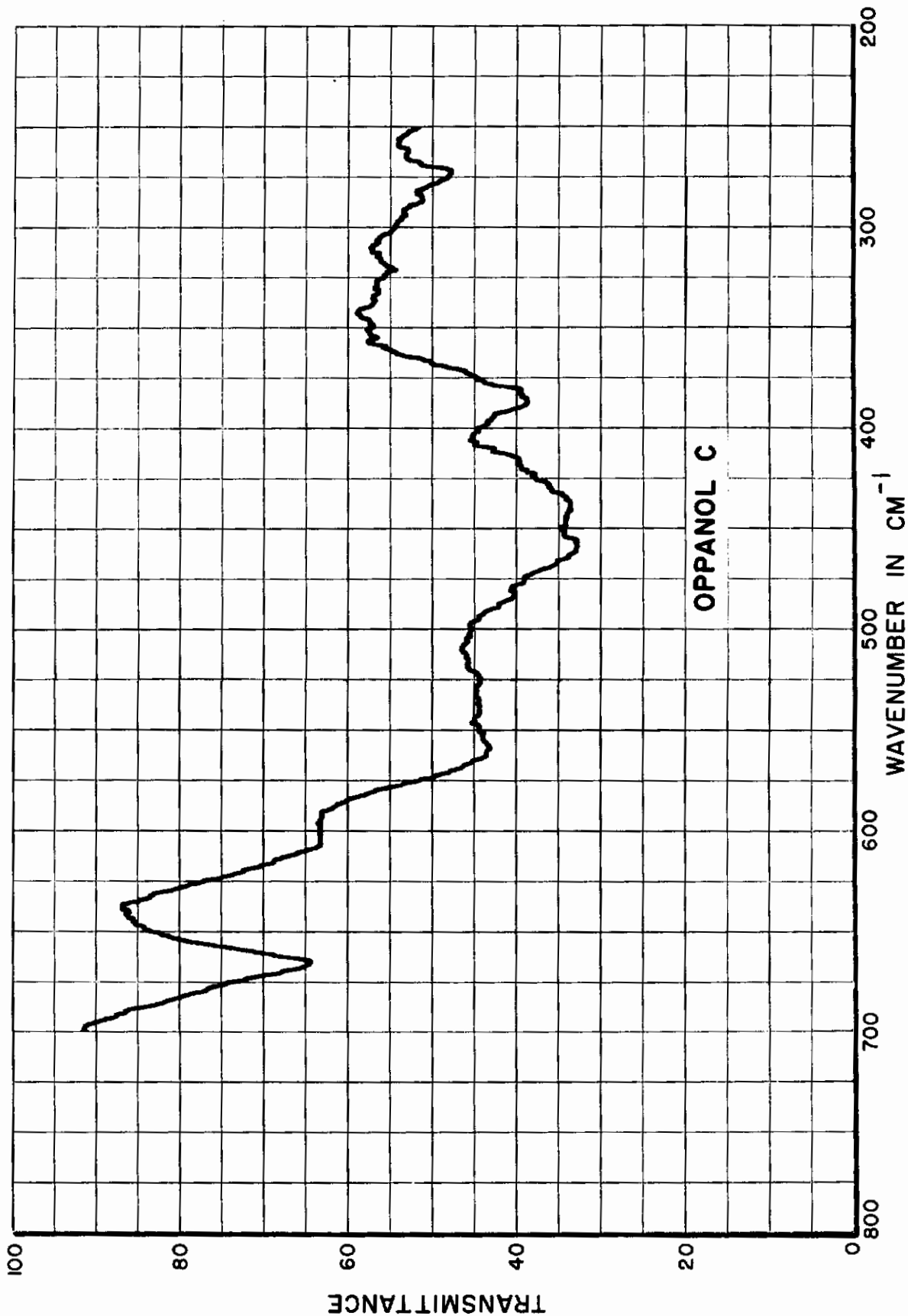


Figure 87. - Infrared Spectrum from 700 - 250  $\text{cm}^{-1}$  of Oppanol C (Polyvinyl Isobutyl Ether) Recorded as a film approximately 0.13 mm in thickness

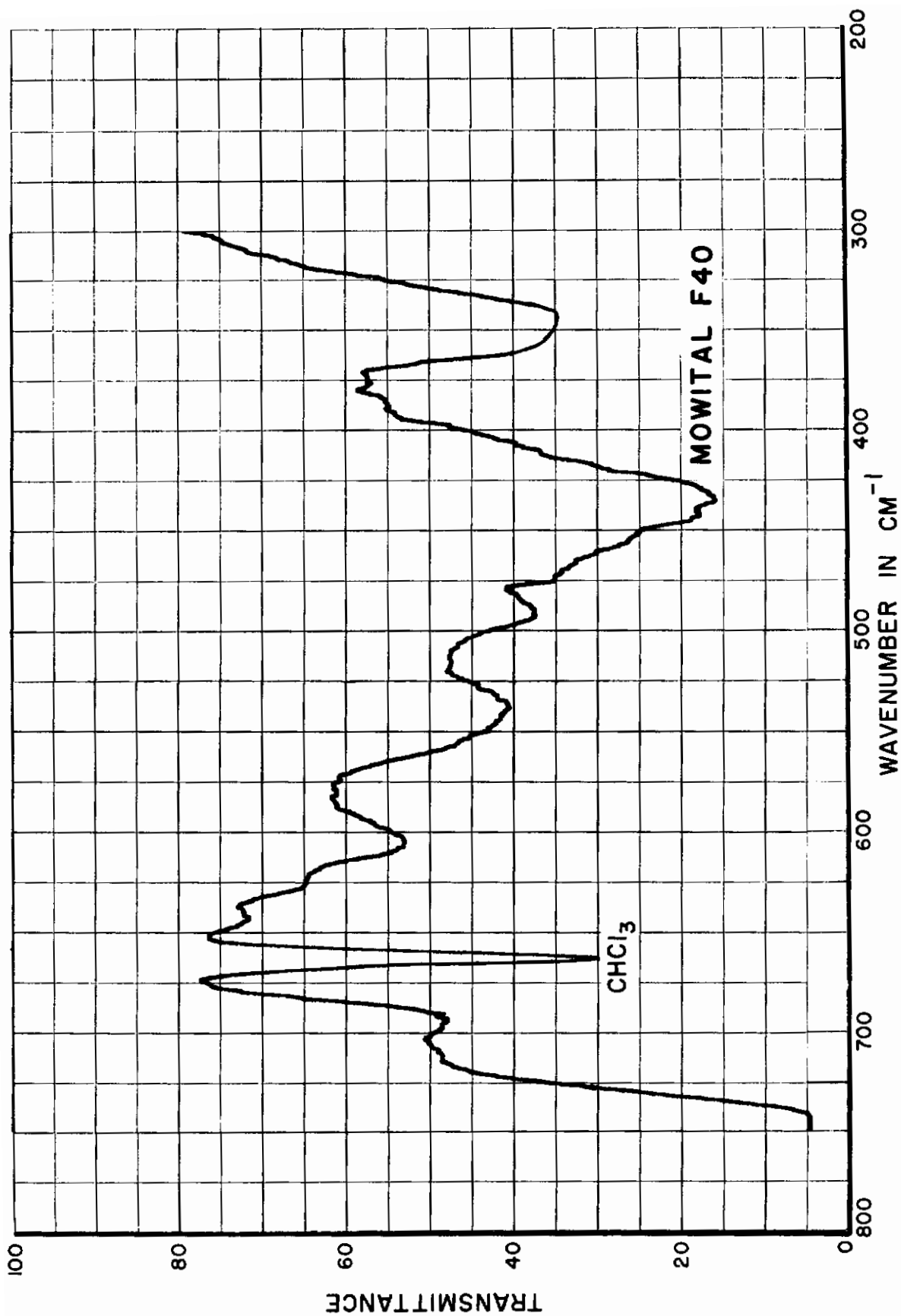


Figure 98. - Infrared Spectrum From 750 - 300 cm<sup>-1</sup> of Mowital F 40 (Polyvinyl Formal)  
Recorded as a film approximately 0.1 mm in thickness, prepared  
from chloroform solution

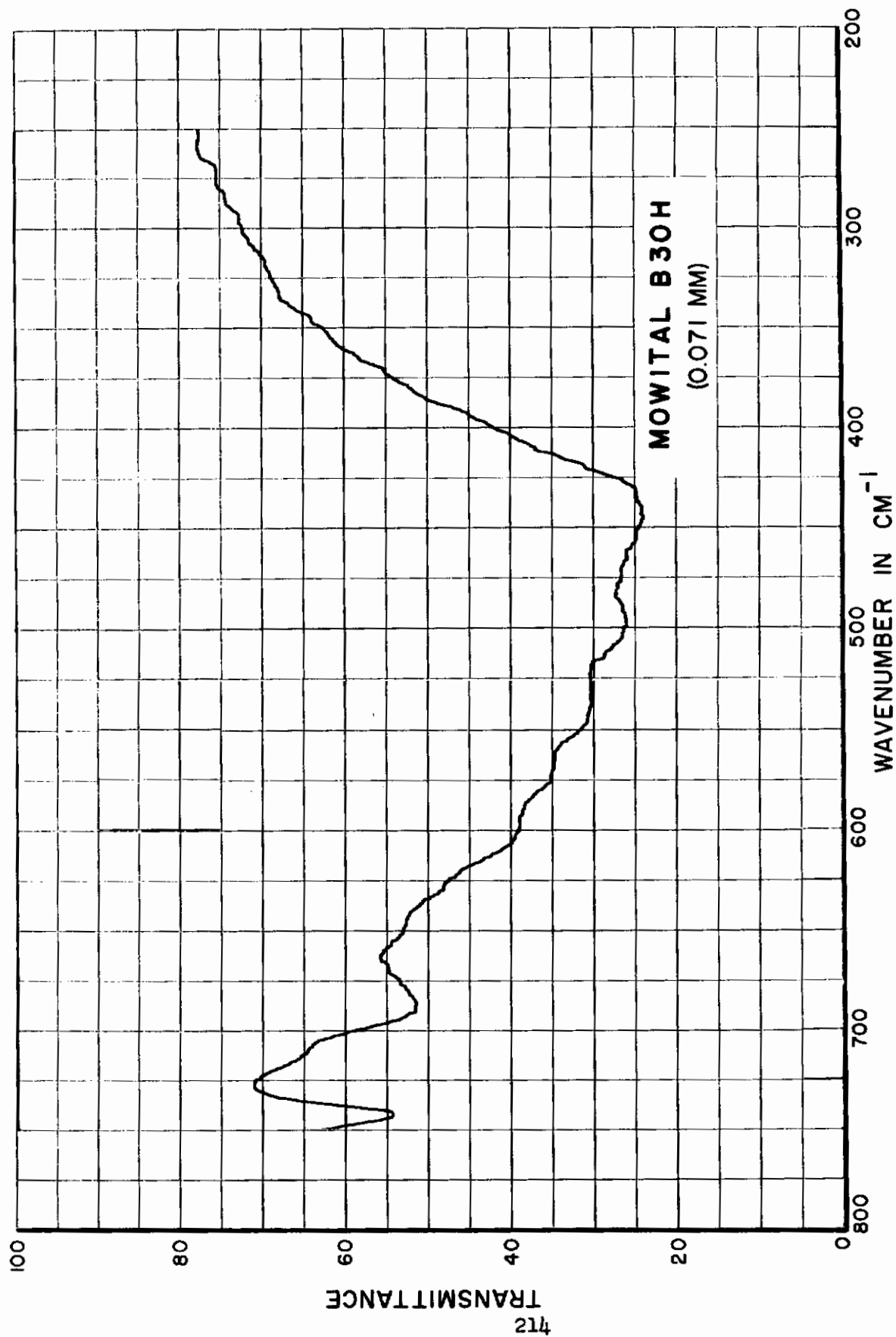


Figure 39. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Mowital B 30 H (Polyvinyl Butyral)  
Recorded as a film 0.07 mm in thickness, prepared from a chloroform solution

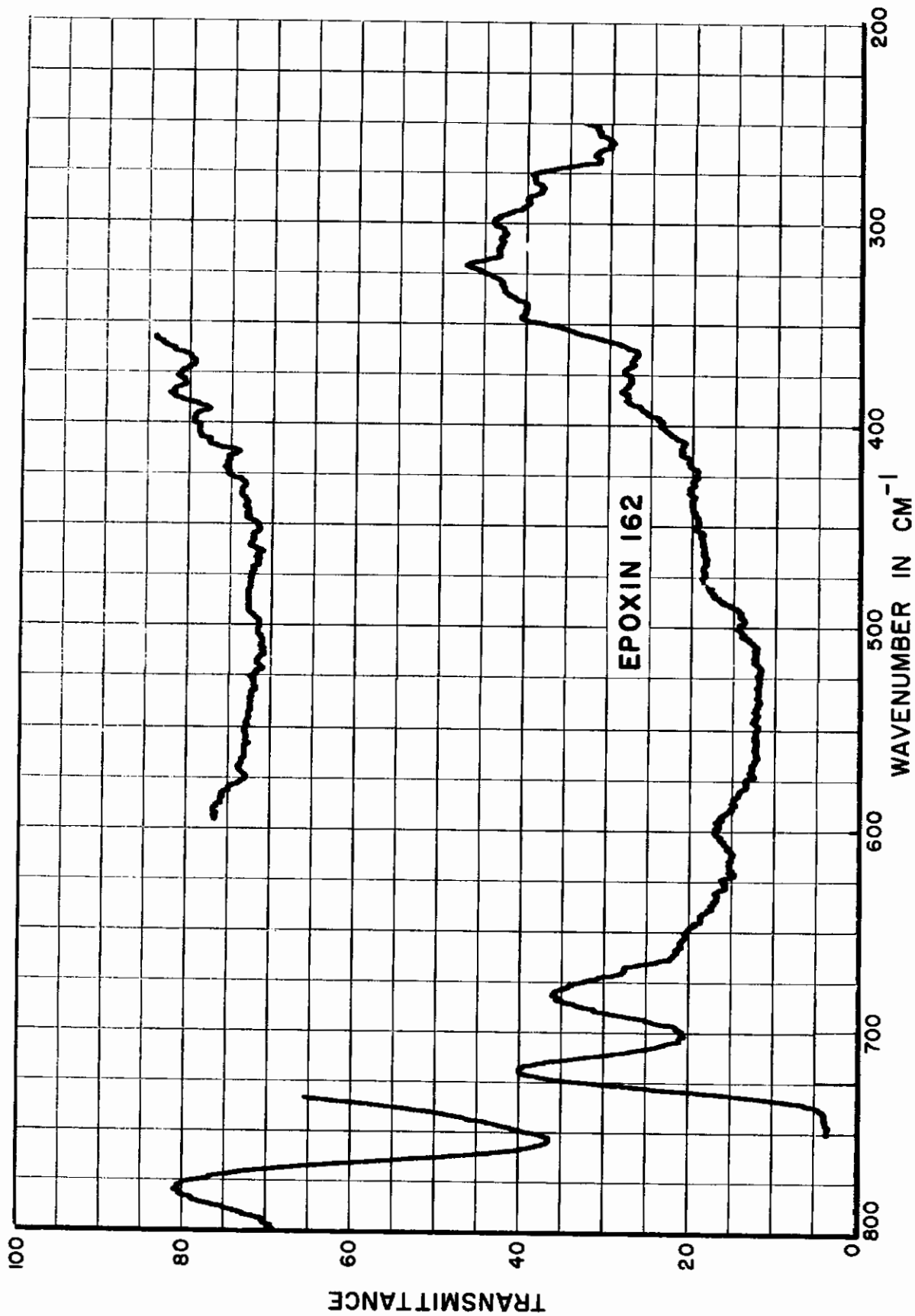


Figure 90. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Epoxin 162 (Aliphatic Epoxy Resin)  
Recorded as a film

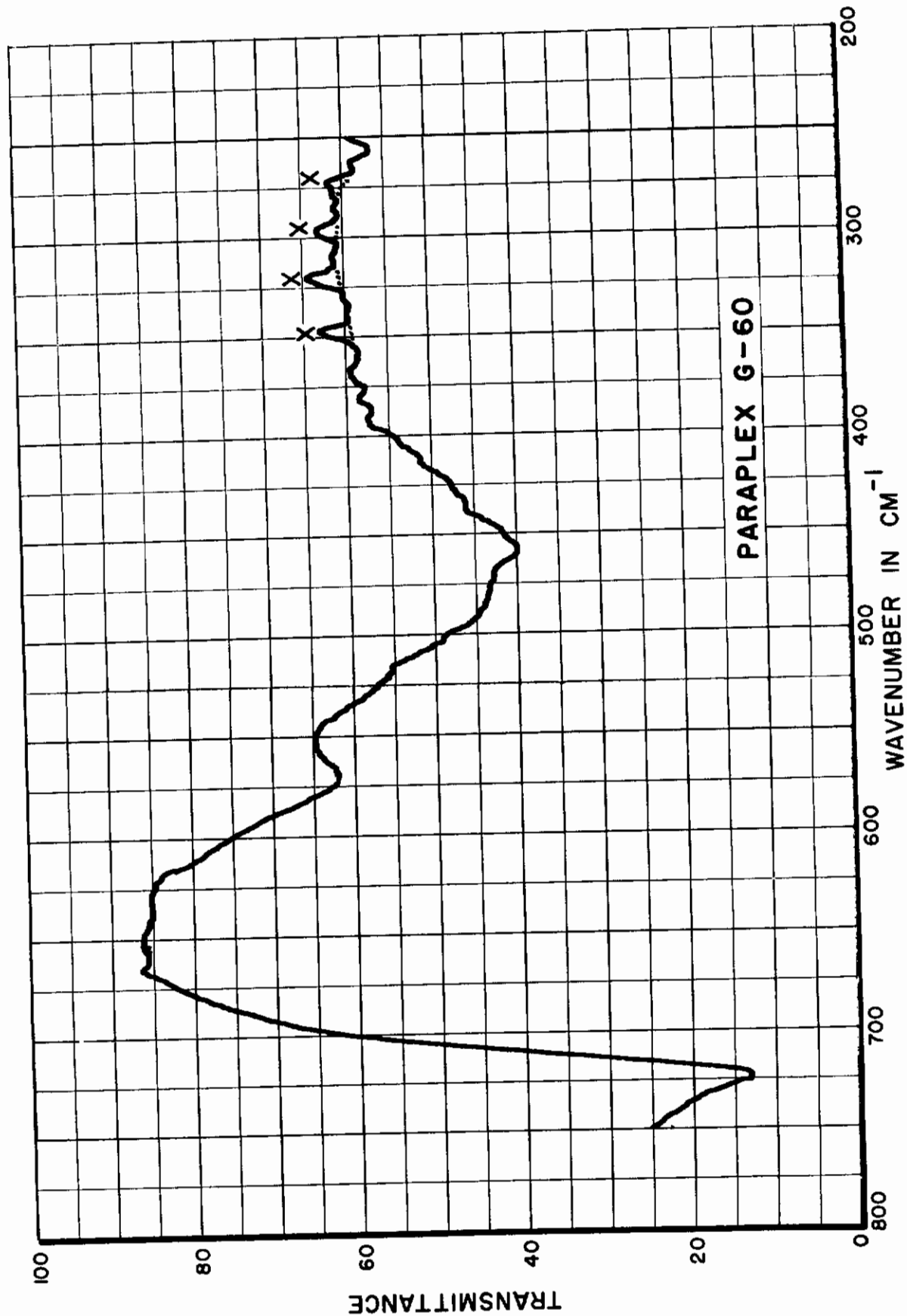


Figure 91. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Paraplex G-60 (Epoxidized Soy-Bean Oil)  
Recorded in a 0.1 mm CsBr cell



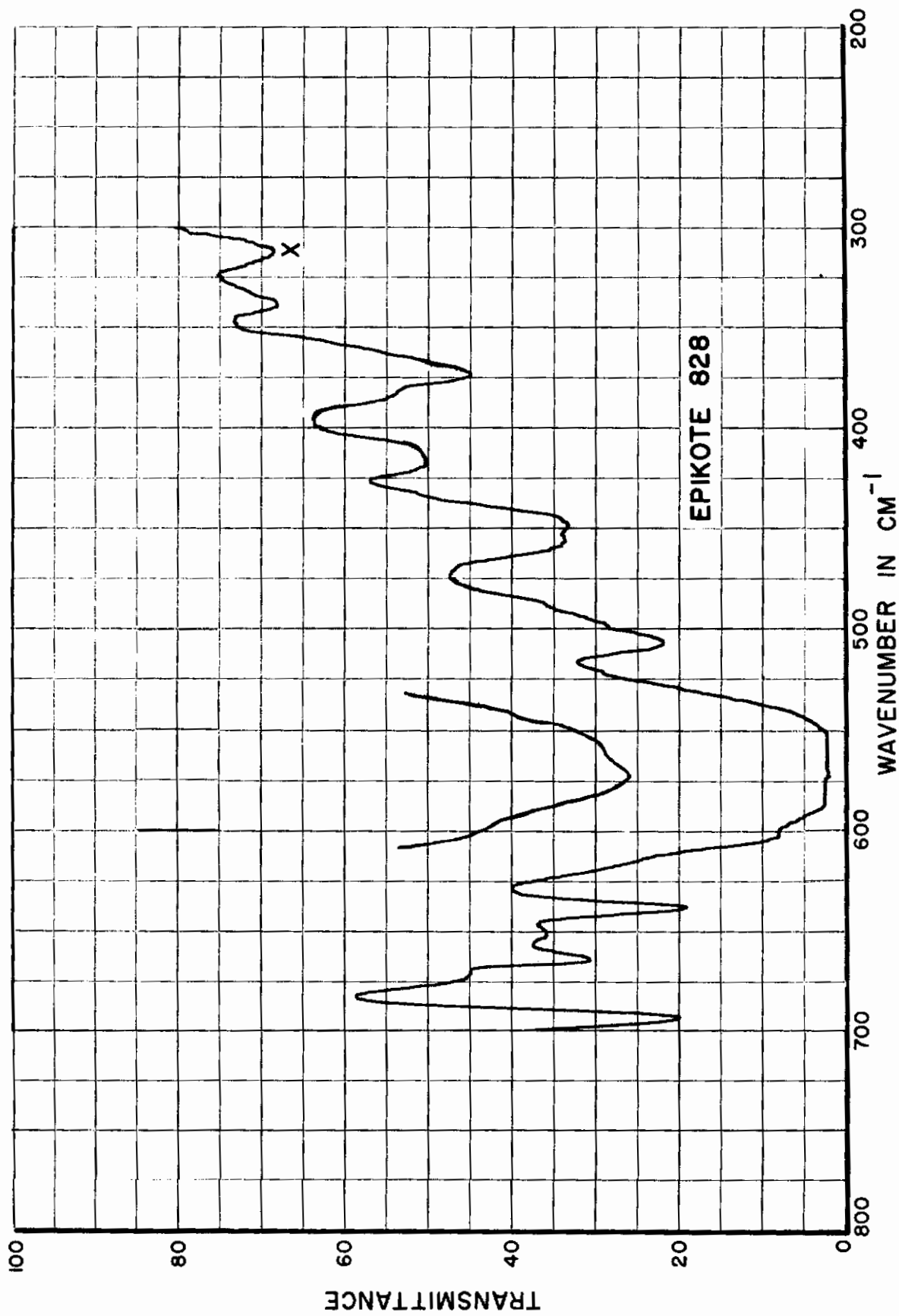


Figure 92. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Epikote 828 (Low Molecular Weight Epoxy Resin on Base of Bisphenol A  
Recorded as a film

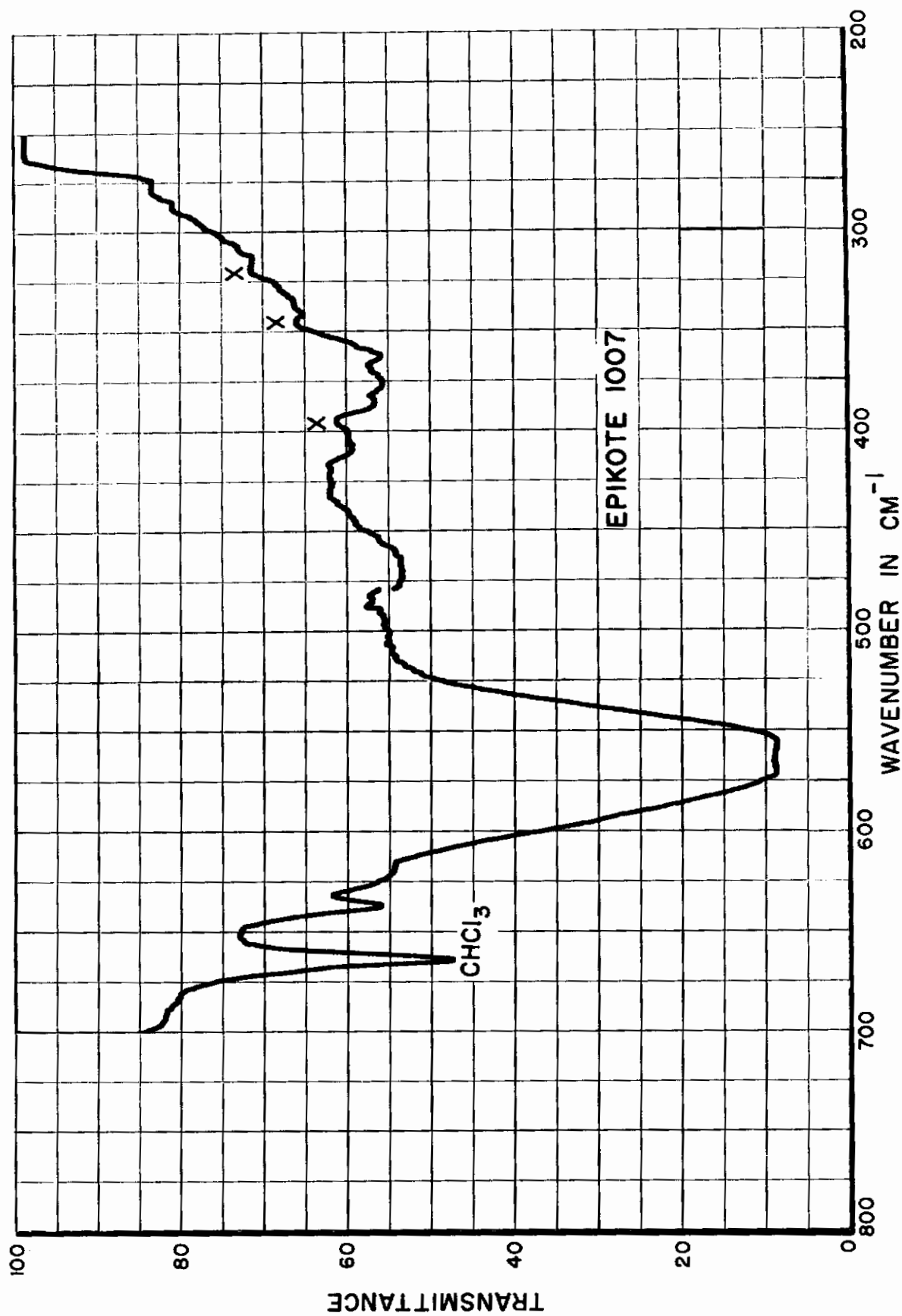


Figure 93. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Epikote 1007 (High Molecular Weight Epoxy Resin on Base of Bisphenol A)

Recorded as a film, prepared from a chloroform solution

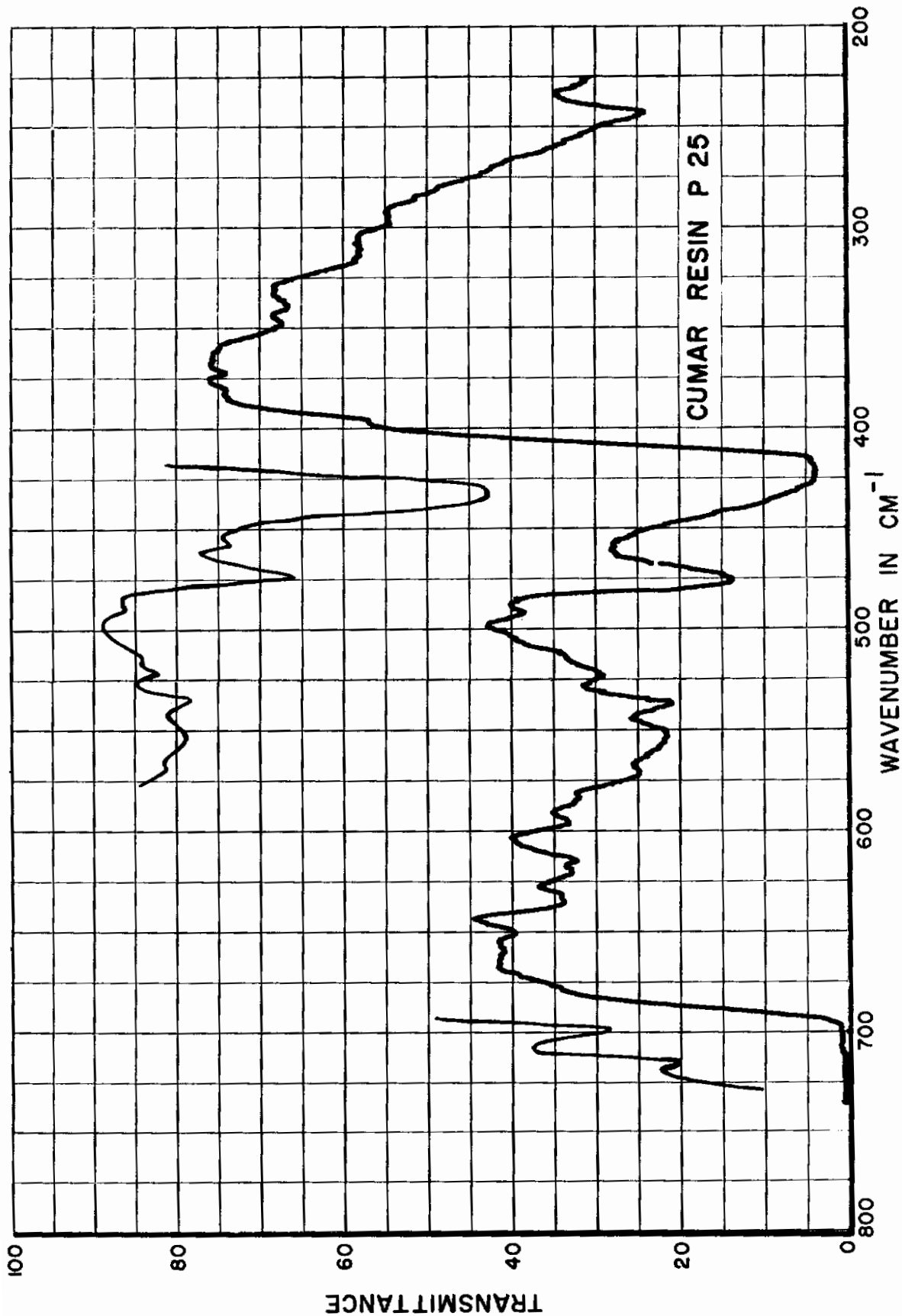


Figure 94. - Infrared Spectrum from 725 - 225  $\text{cm}^{-1}$  of Cumar Resin P 25 (Probably Indene-Coumarone Resin)

Recorded as a film

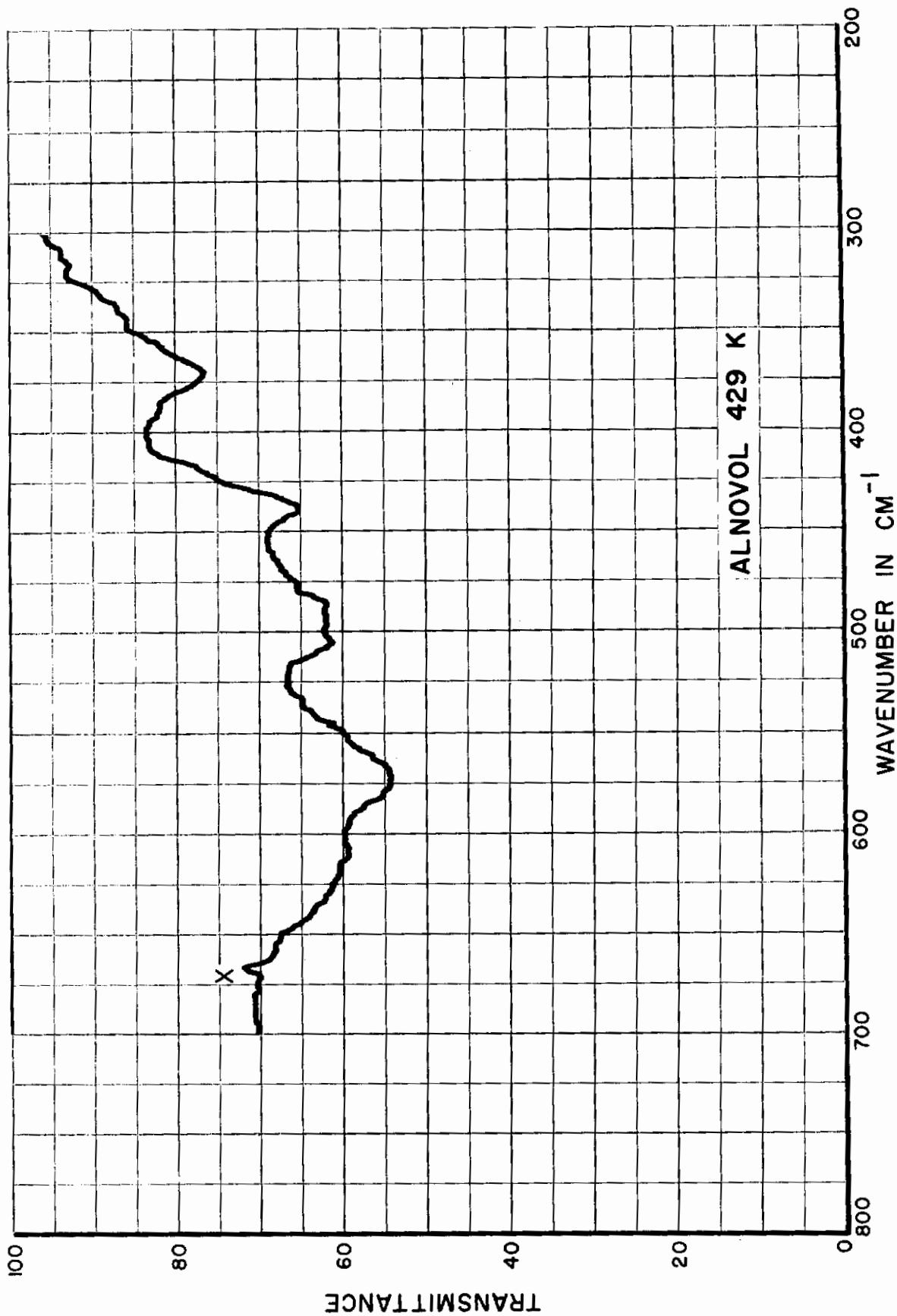


Figure 95. - Infrared Spectrum from 725 - 300 cm<sup>-1</sup> of Alnovol 429 K (Cresol Novolac)  
Recorded as a film, prepared from isopropanol solution

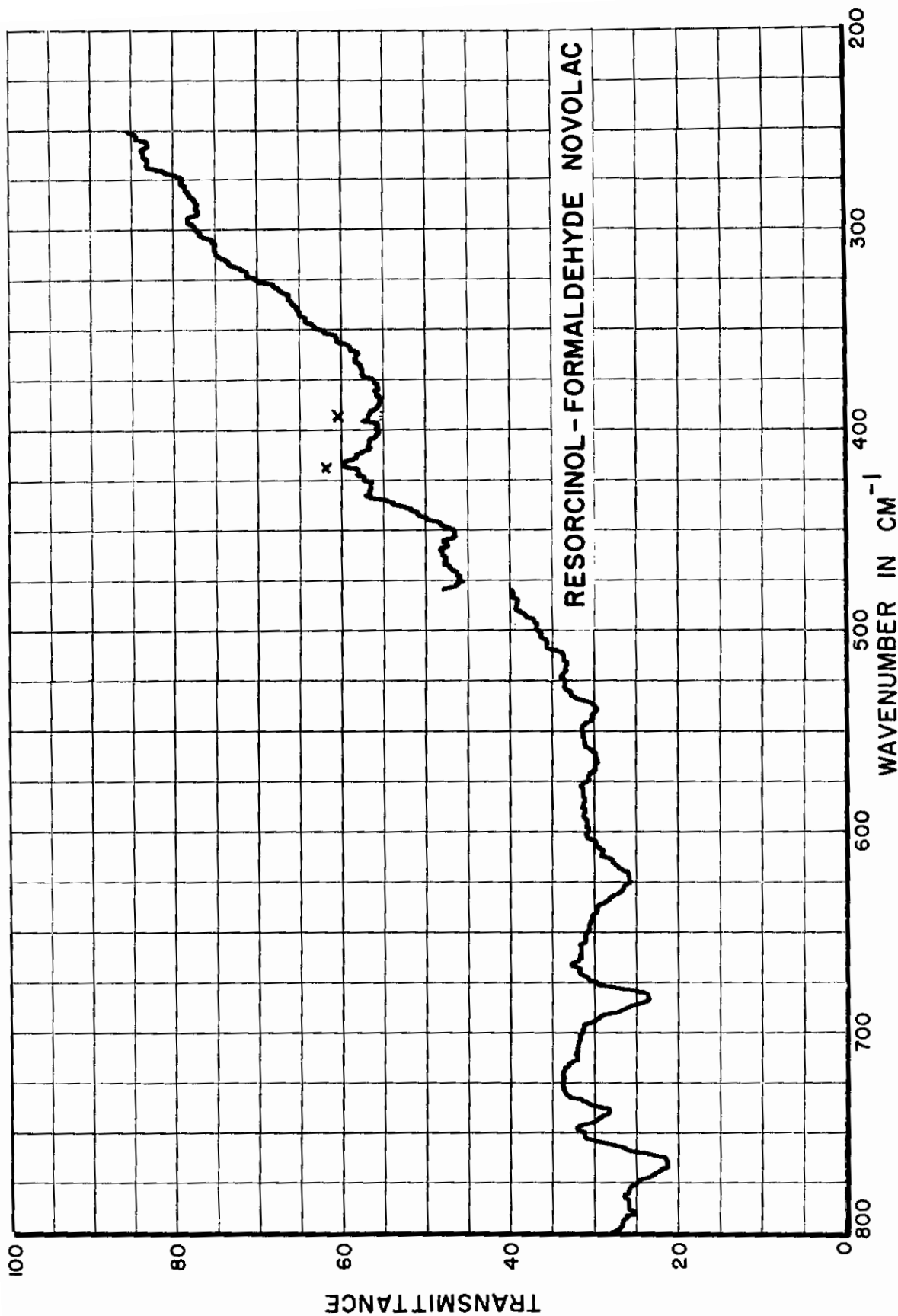


Figure 96. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Resorcinol-Formaldehyde Novolac  
Recorded as a film, prepared from isopropanol solution

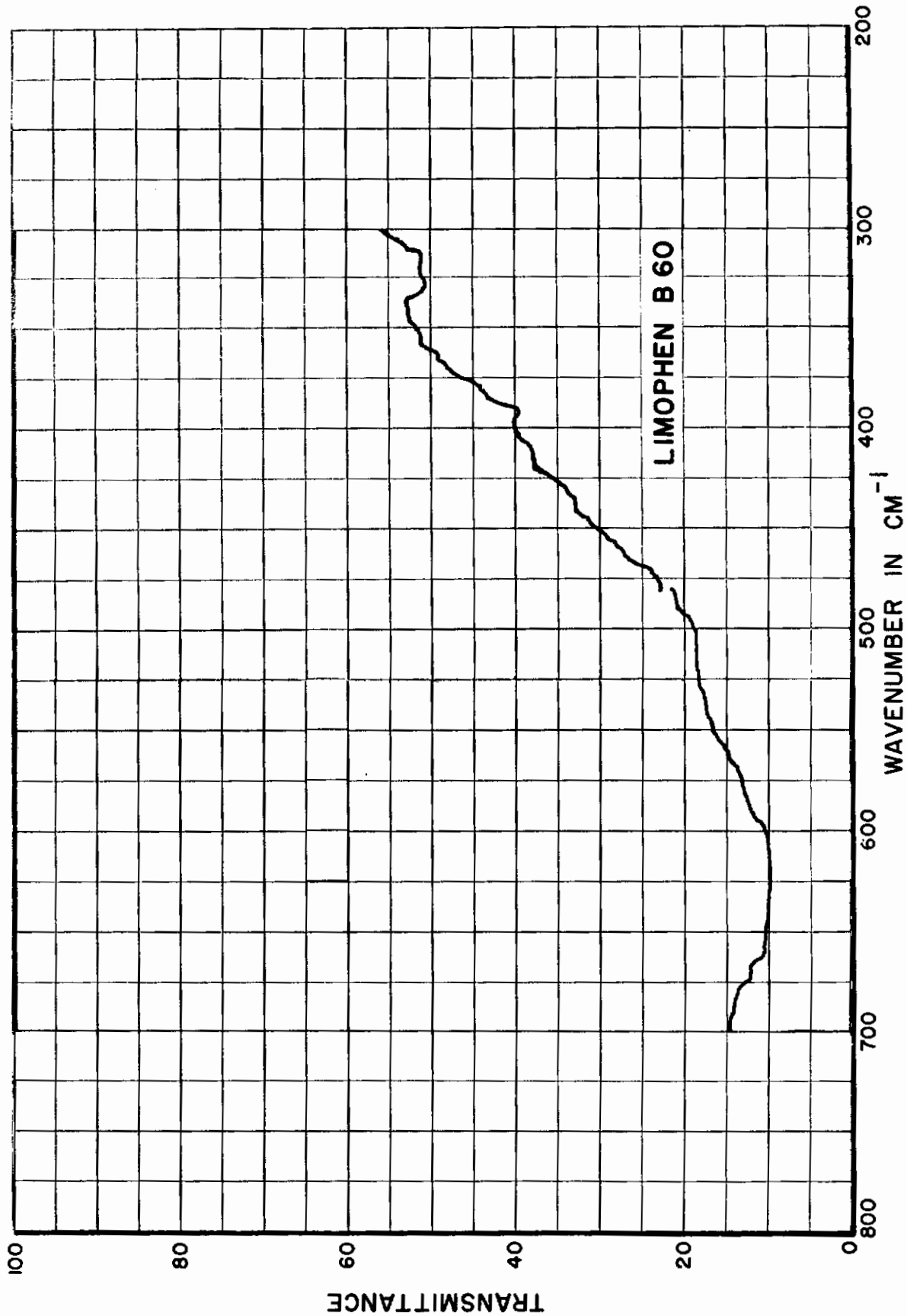


Figure 97. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Limophen B 60 (Phenol Resole)  
Recorded as a film from solution

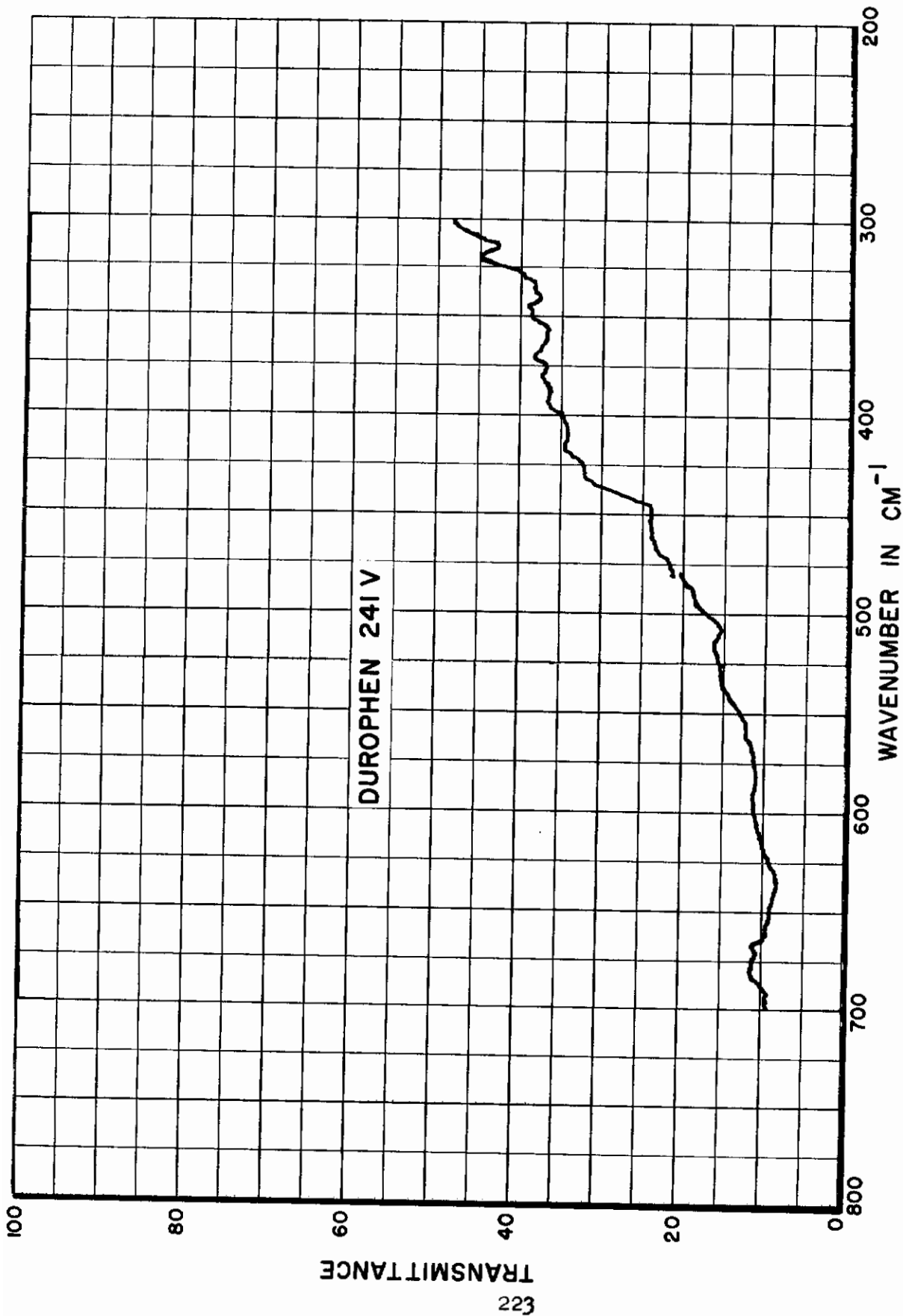


Figure 98. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Durophen 241 V (Plasticized Phenol Resole)  
Recorded as a film from solution

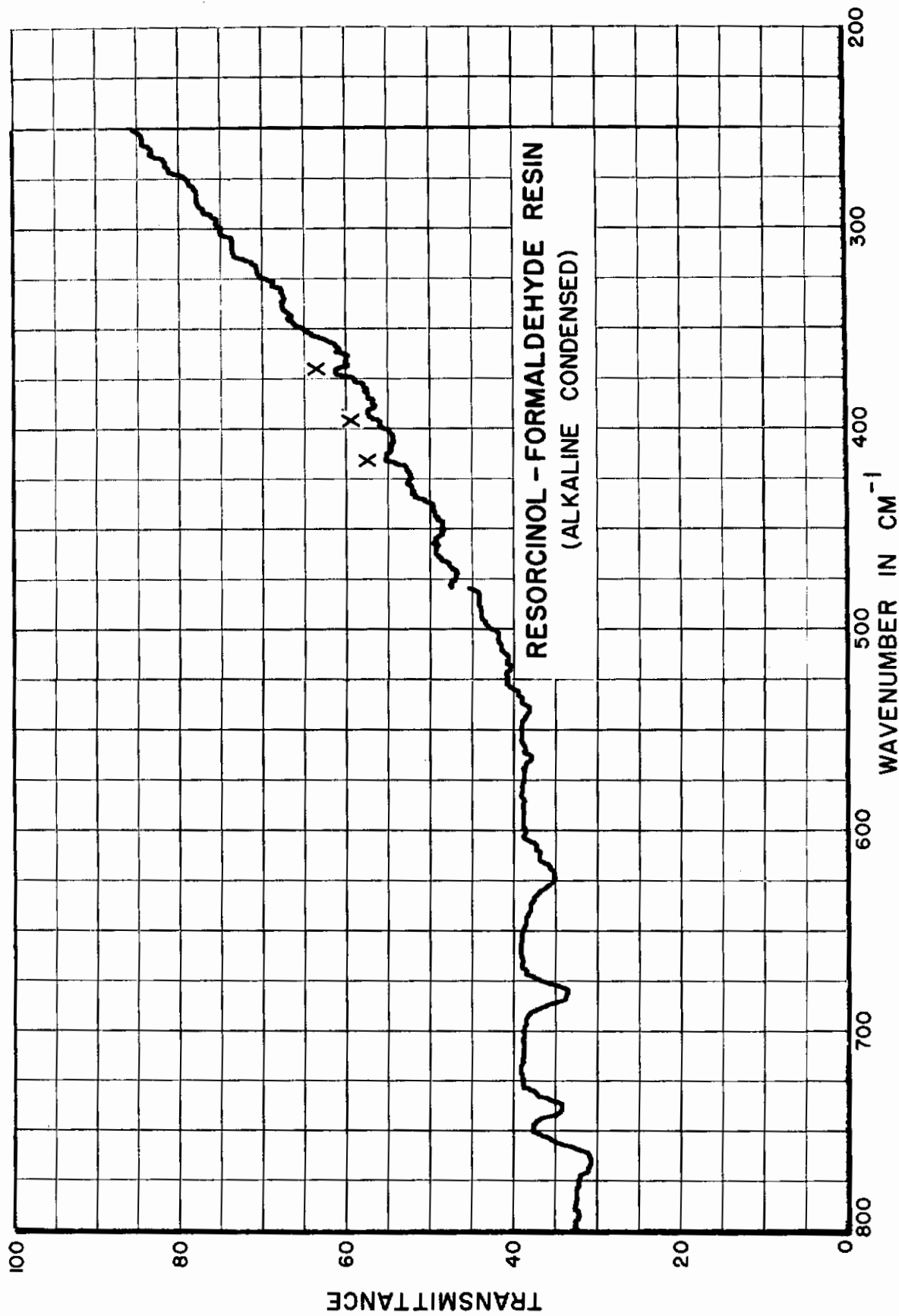


Figure 99. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Resorcinol-Formaldehyde Resin (Alkaline-Condensed)

Recorded as a film, prepared from isopropanol solution

422



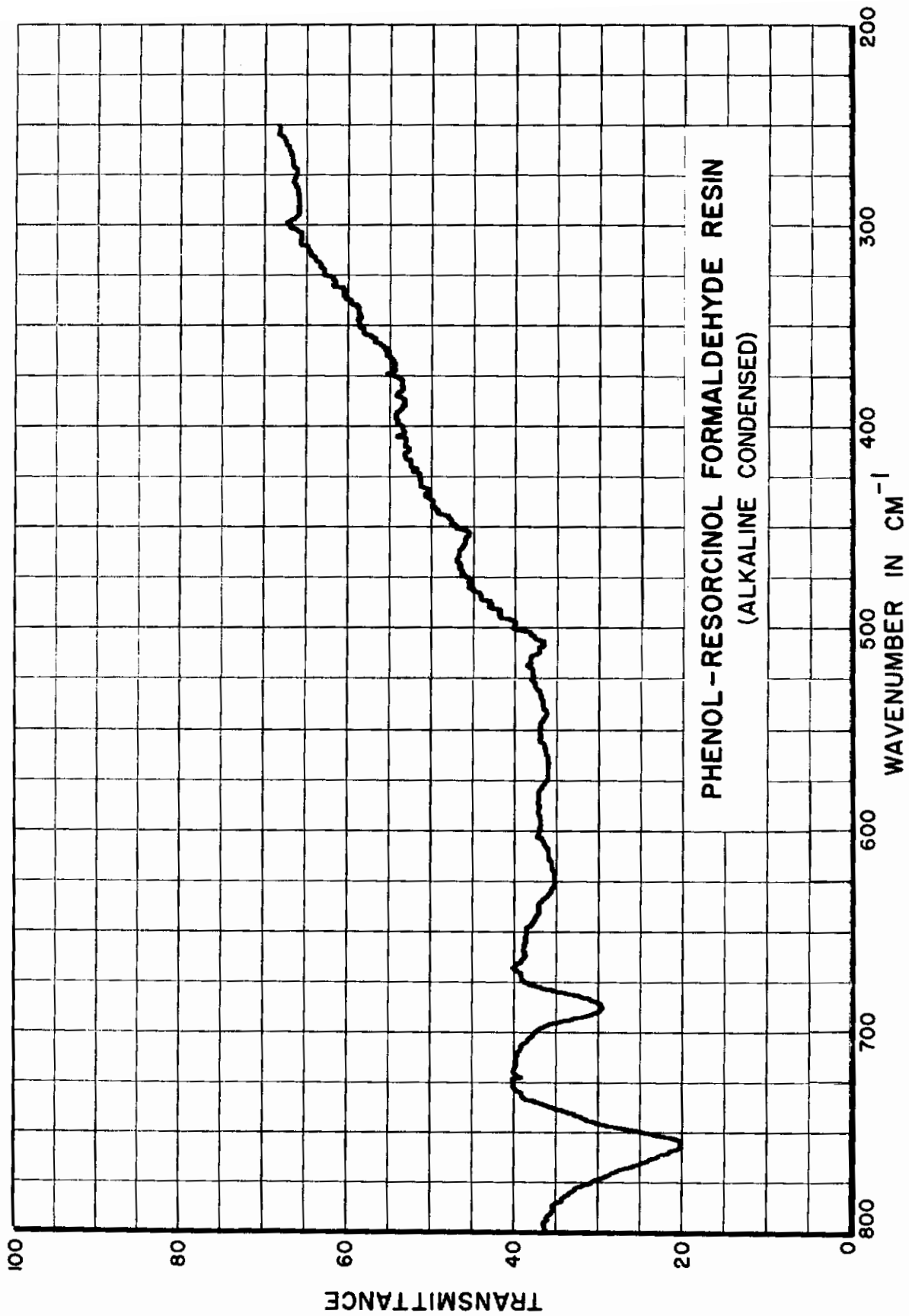


Figure 100. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Phenol-Resorcinol Formaldehyde Resin (Alkaline Condensed)  
Recorded as a film, prepared from isopropanol solution

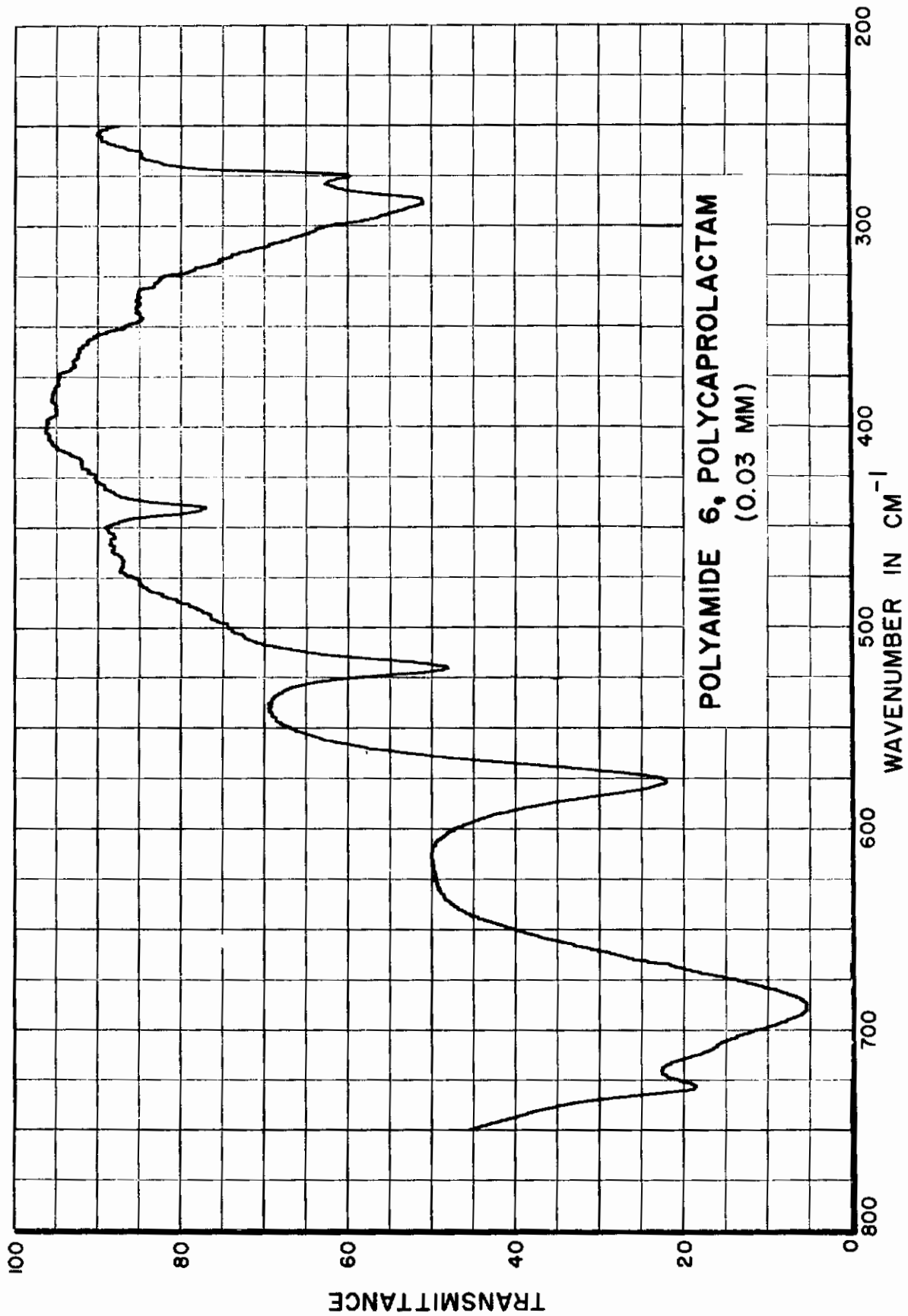


Figure 101. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Polyamide 6, Polycaprolactam (Durethan BK) Recorded as a film 0.03 mm in thickness, prepared from a formic acid solution

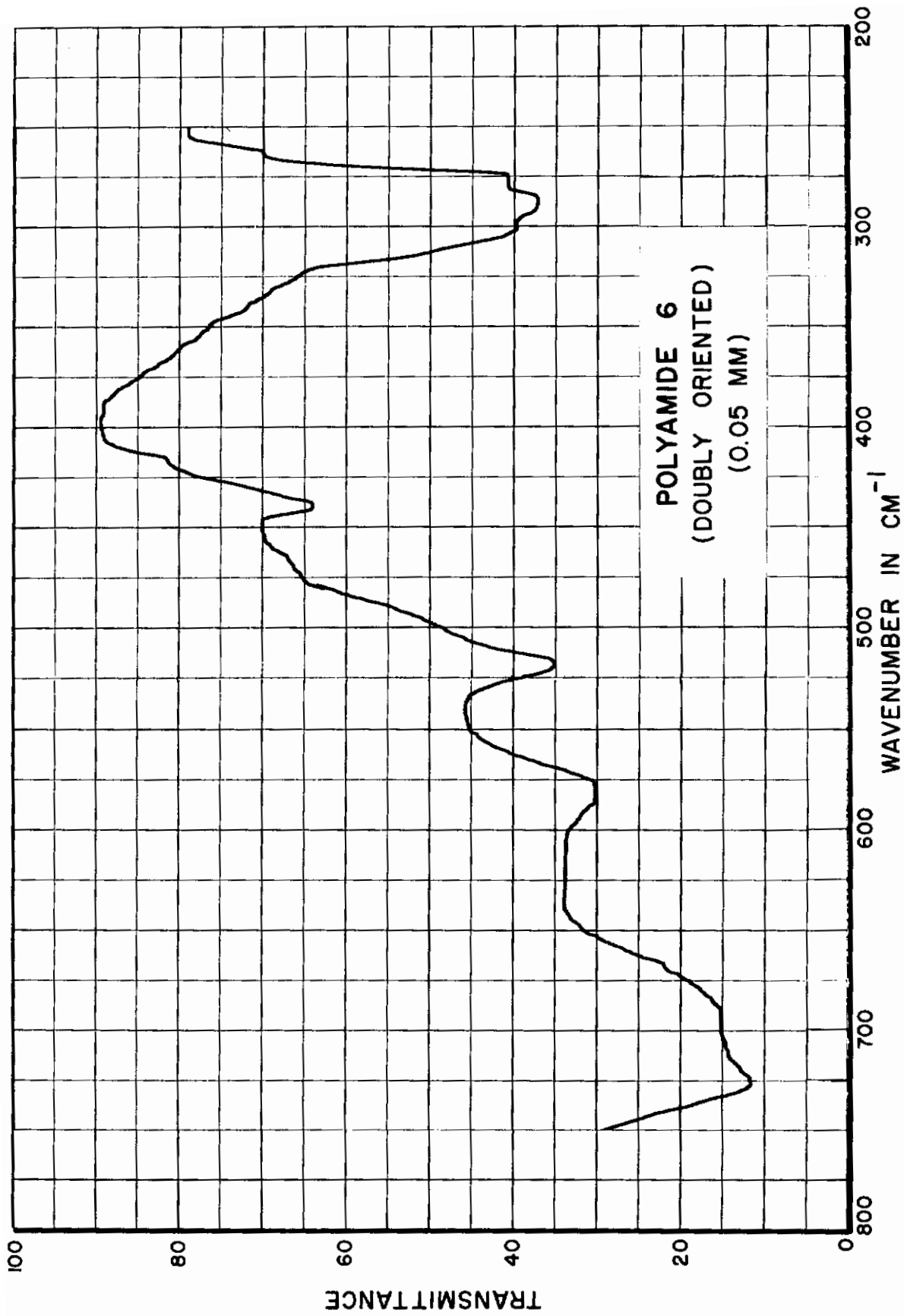


Figure 102. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Polyamide 6, Polycaprolactam (Biaxially Oriented)

Recorded as a film 0.05 mm in thickness

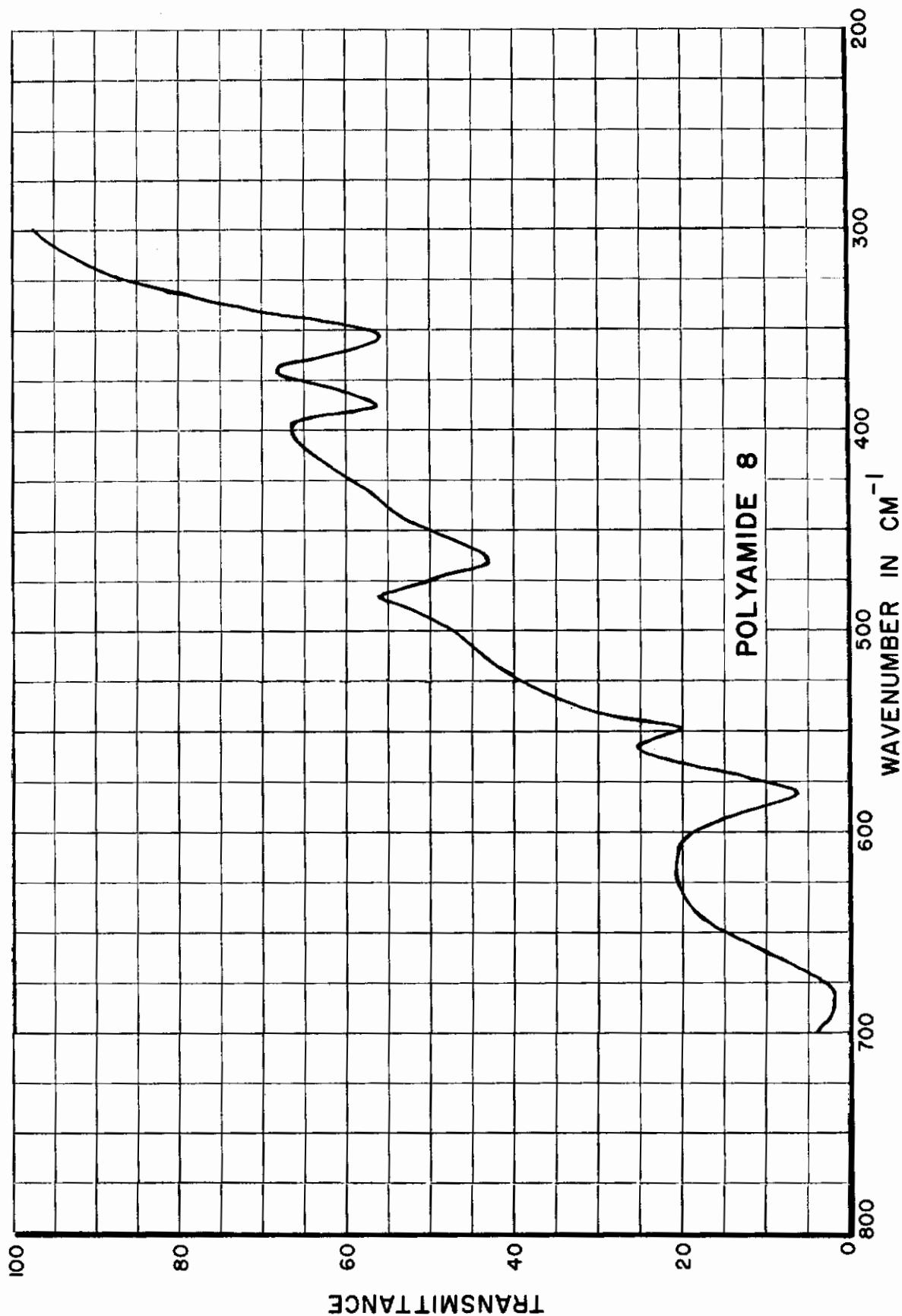


Figure 103. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Polyamide 8 (Polycapryllactam)  
Recorded as a film, prepared from formic acid solution

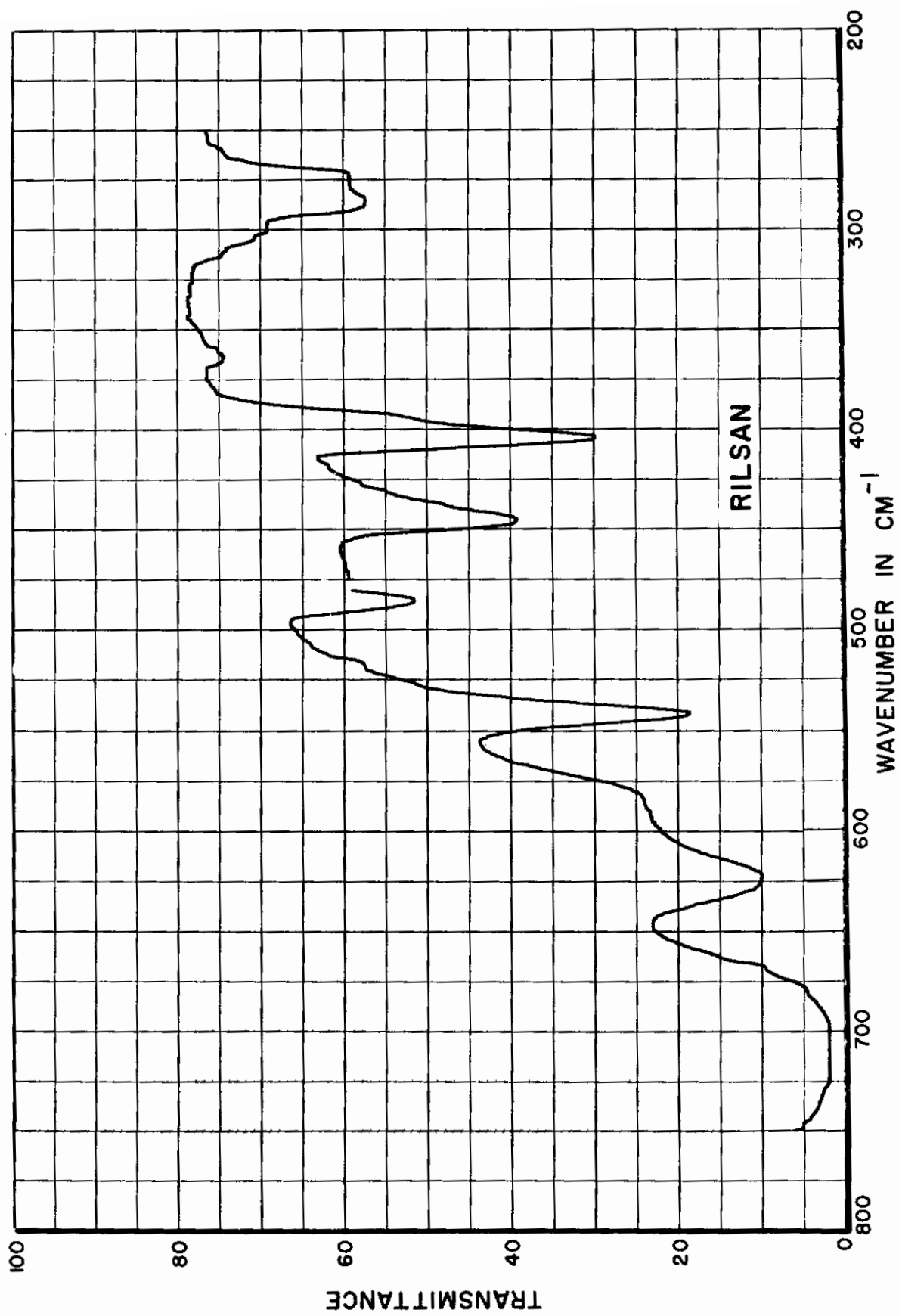


Figure 104. - Infrared Spectrum from 750 - 250  $\text{cm}^{-1}$  of Rilsan (Polyamid 11 or Polyundecyllactam) Recorded as a film approximately 0.2 mm in thickness, prepared from a formic acid solution

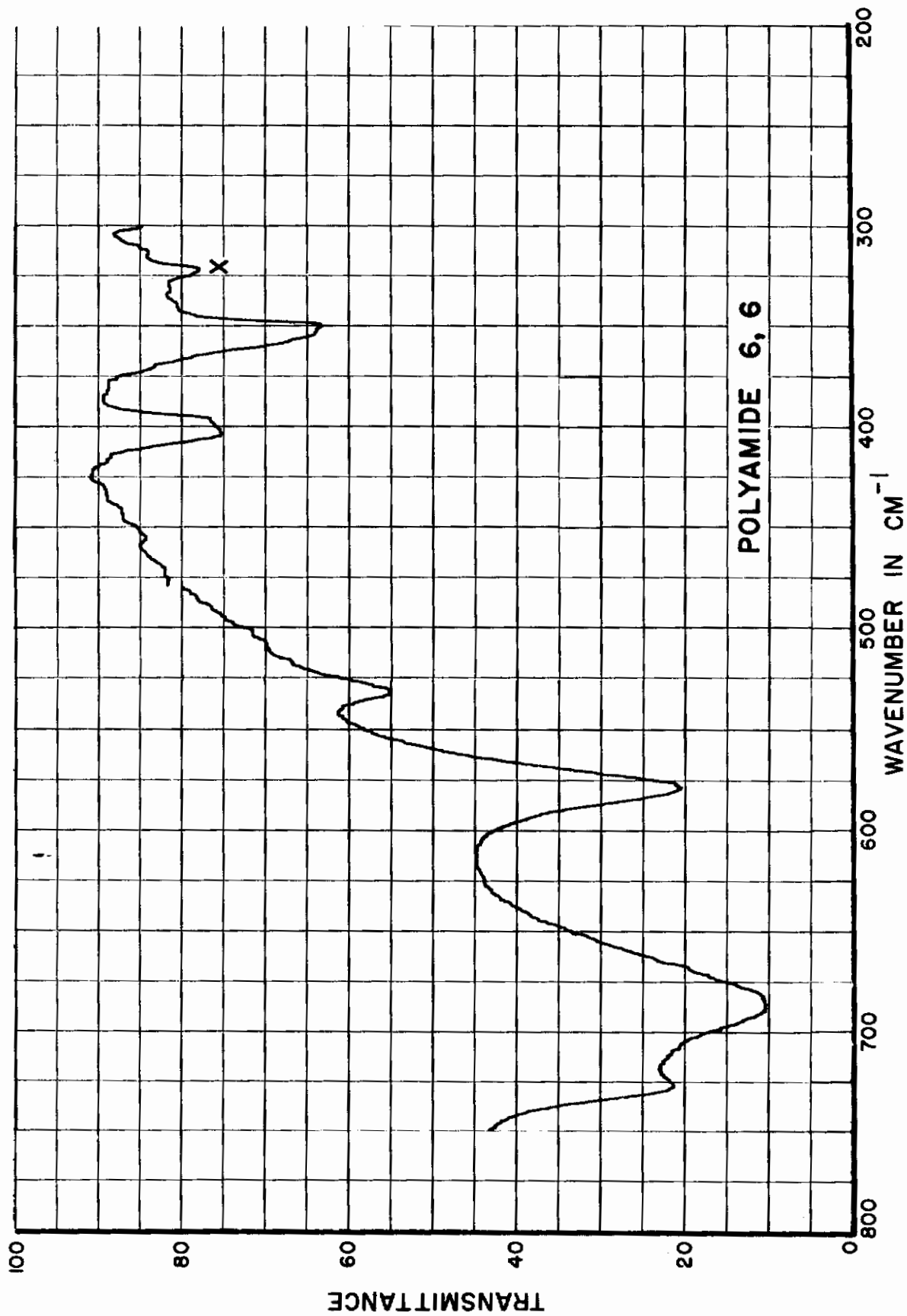


Figure 105. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Polyamid 6,6  
Recorded as a film approximately 0.04 mm in  
thickness, prepared from a formic acid solution

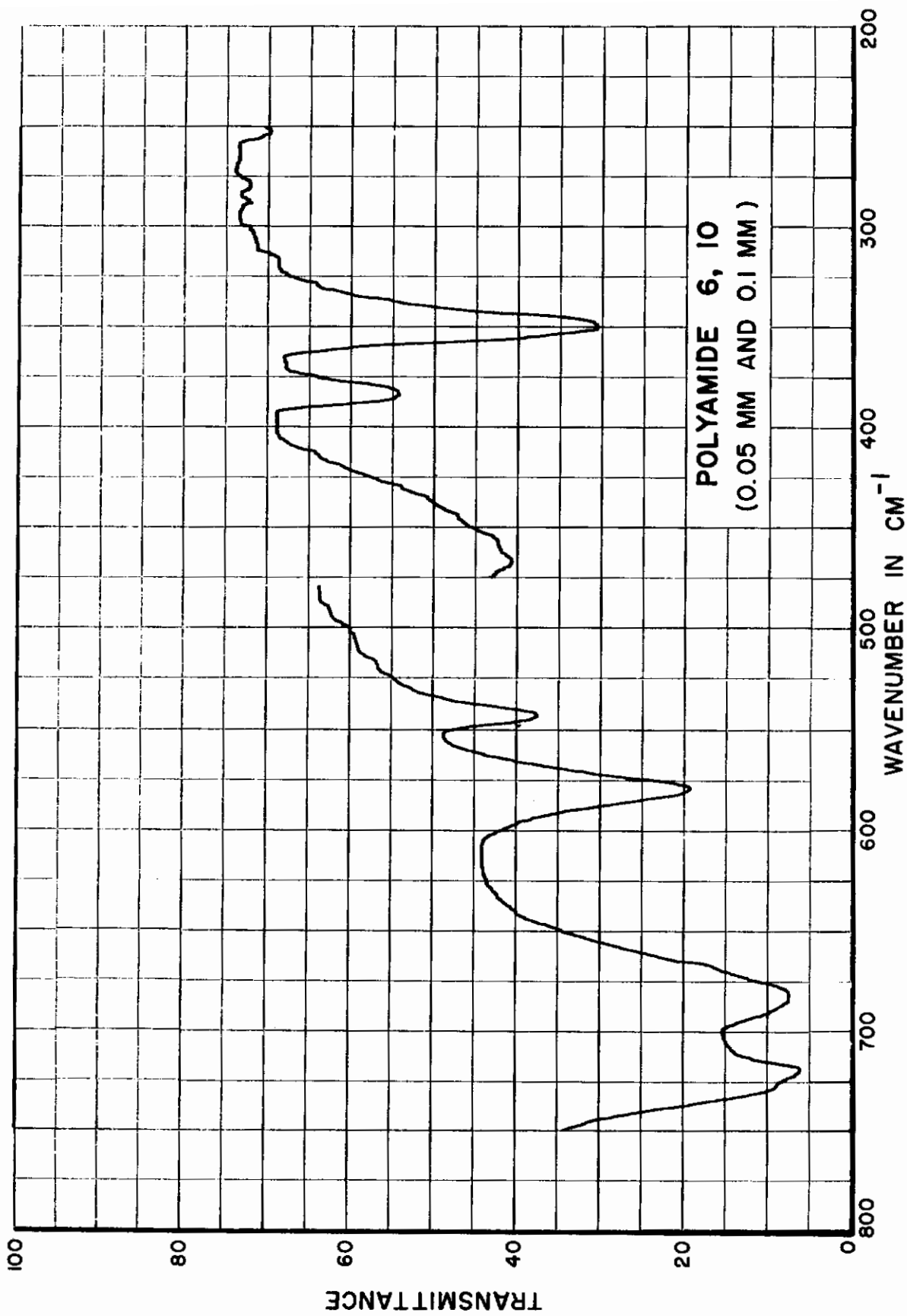


Figure 106. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Polyamide 6,10  
Recorded as films approximately 0.05 mm and 0.1 mm  
in thickness, prepared from a formic acid solution

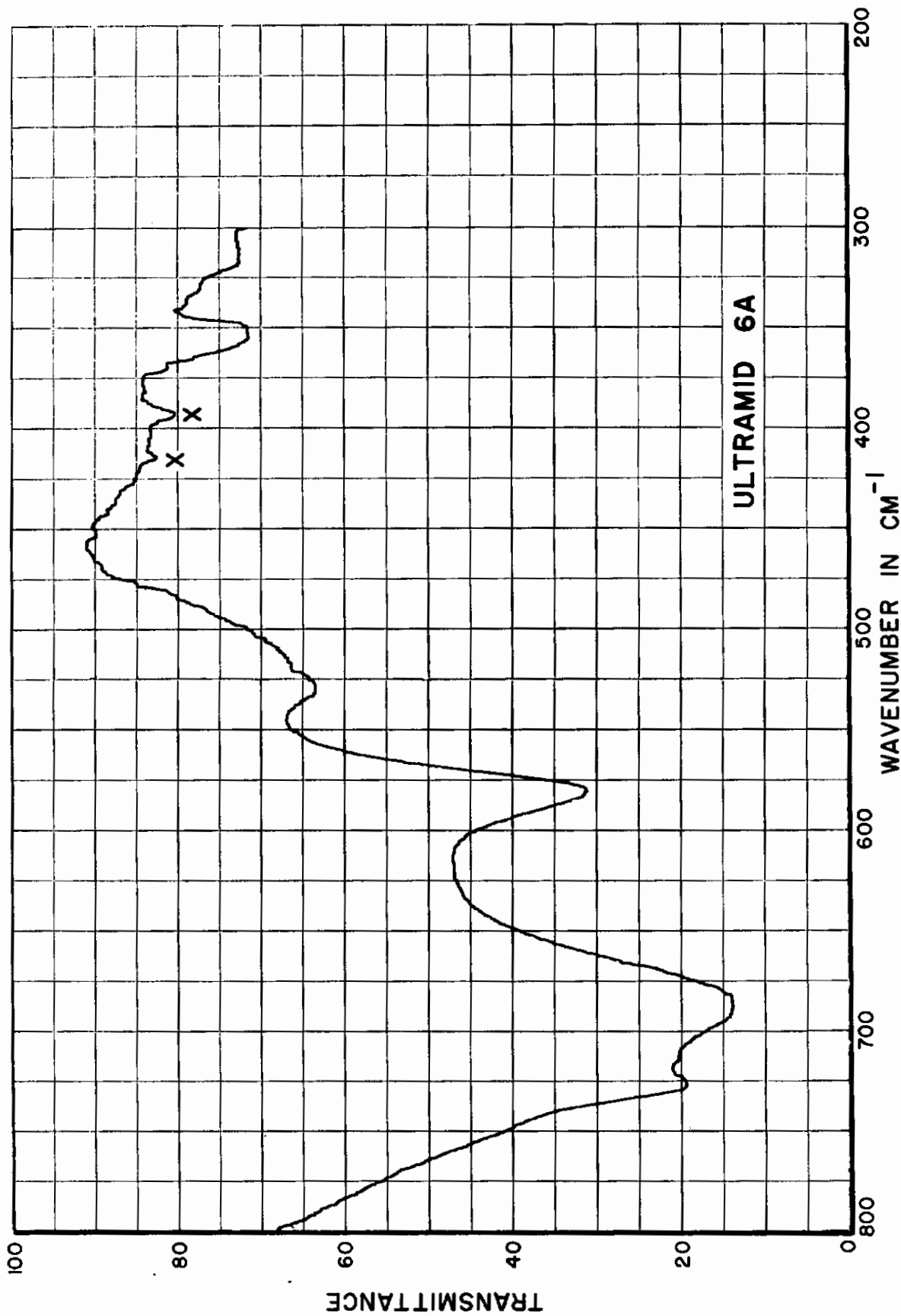


Figure 107. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Ultramid 6A (Copolyamid 6+6,6) Recorded as a film approximately 0.03 mm in thickness, prepared from a formic acid solution



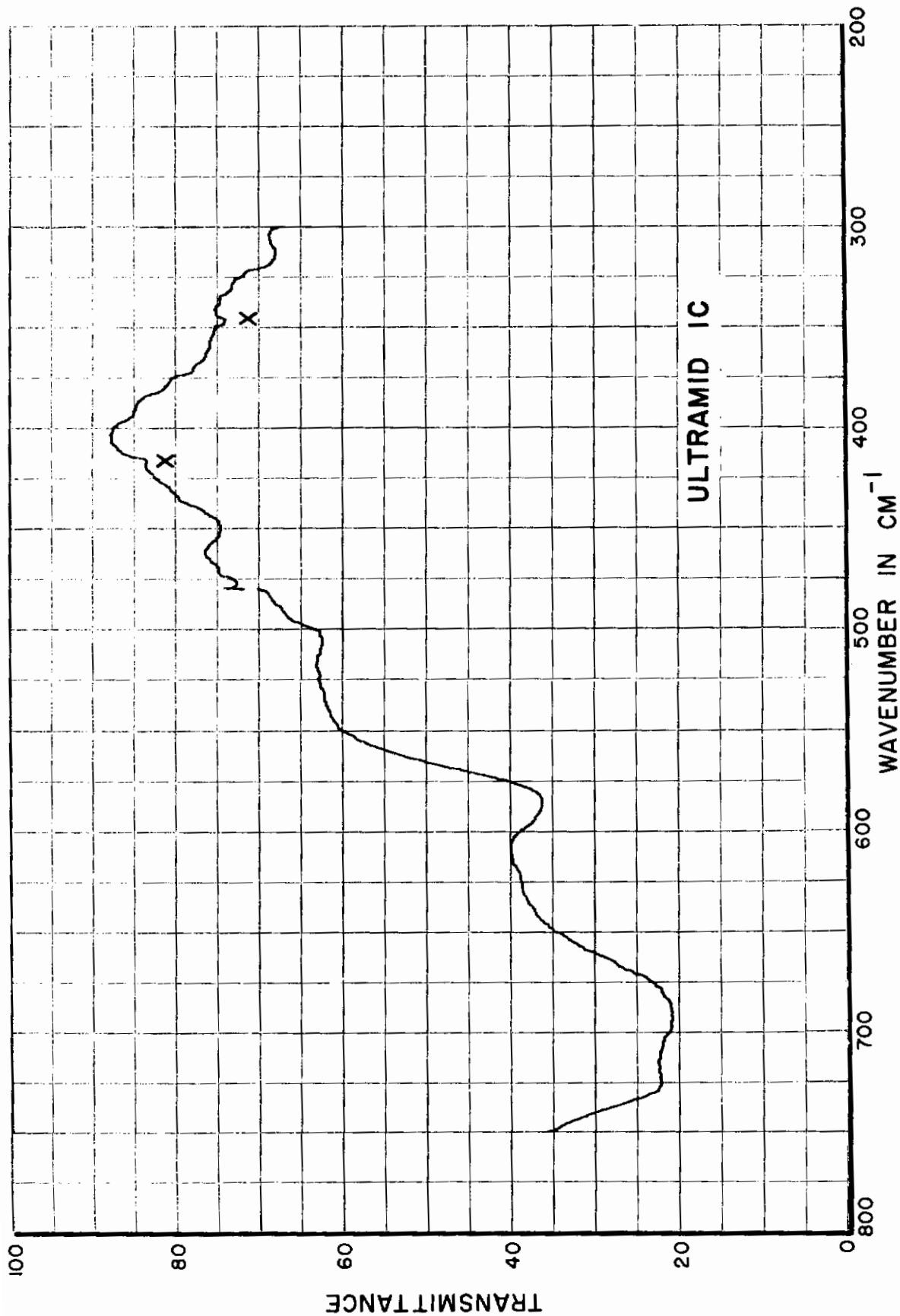


Figure 108. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Ultramid C (Terpolyamide 6+6, 6 - Diimino-dicyclohexylmethane Adipate)

Recorded as a film approximately 0.04 mm in thickness, prepared from a methanol-benzene solution(7:3)

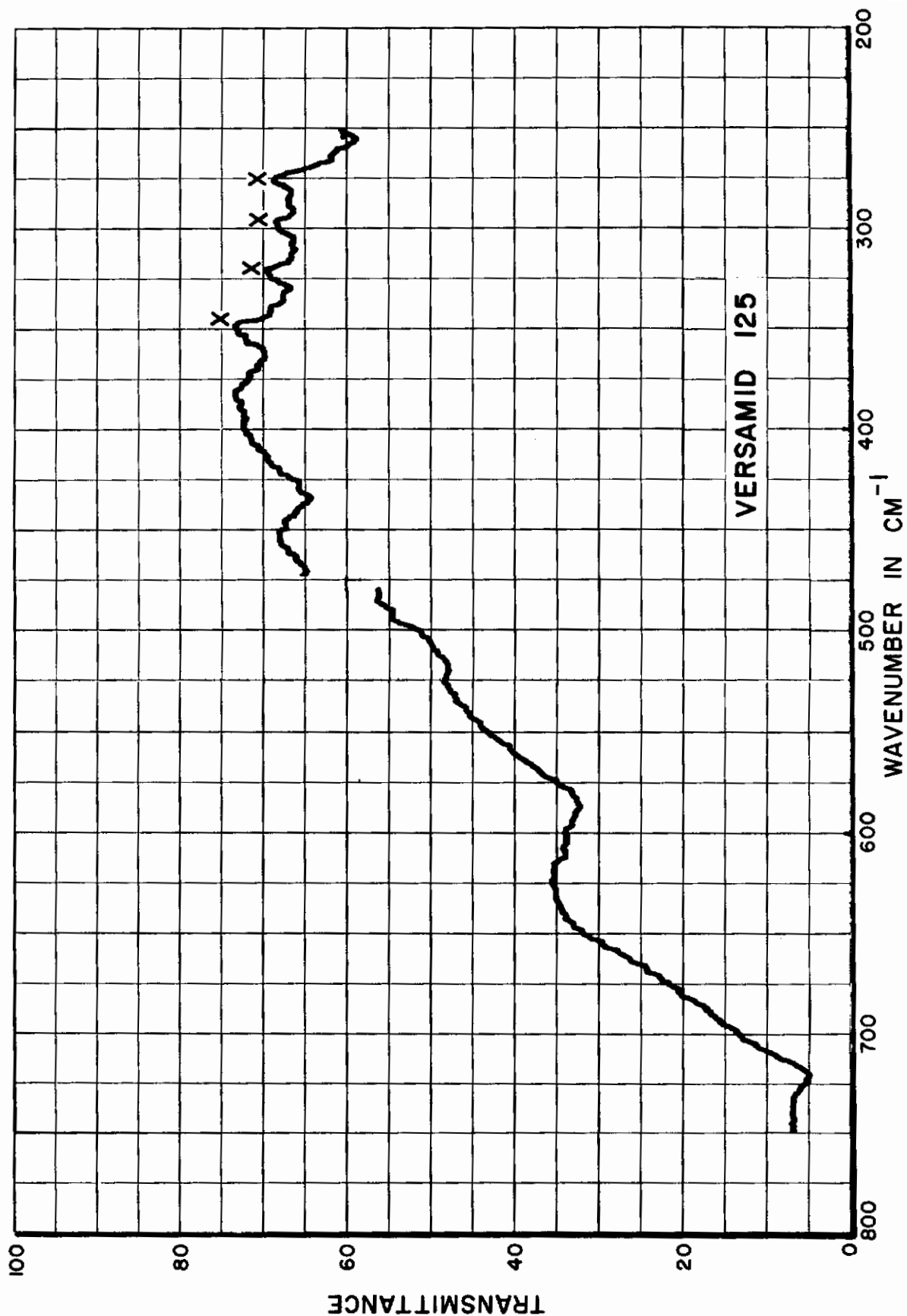


Figure 109. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Versamid 125 (Polyamid from Di- and Trimerized Fatty Acids and a Diamine)  
Recorded as a film

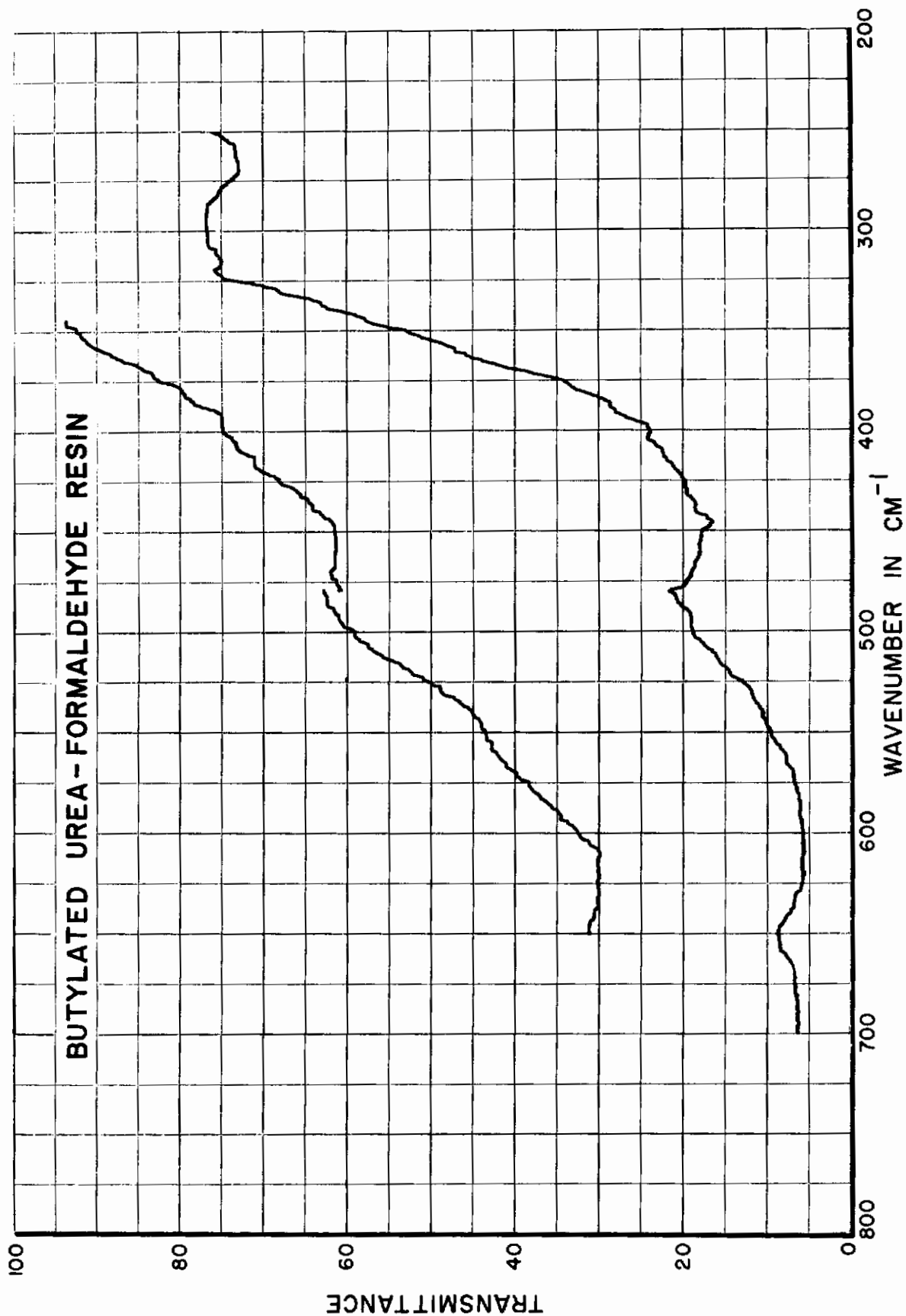


Figure 110. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Butylated Urea-Formaldehyde Resin  
Recorded as a film

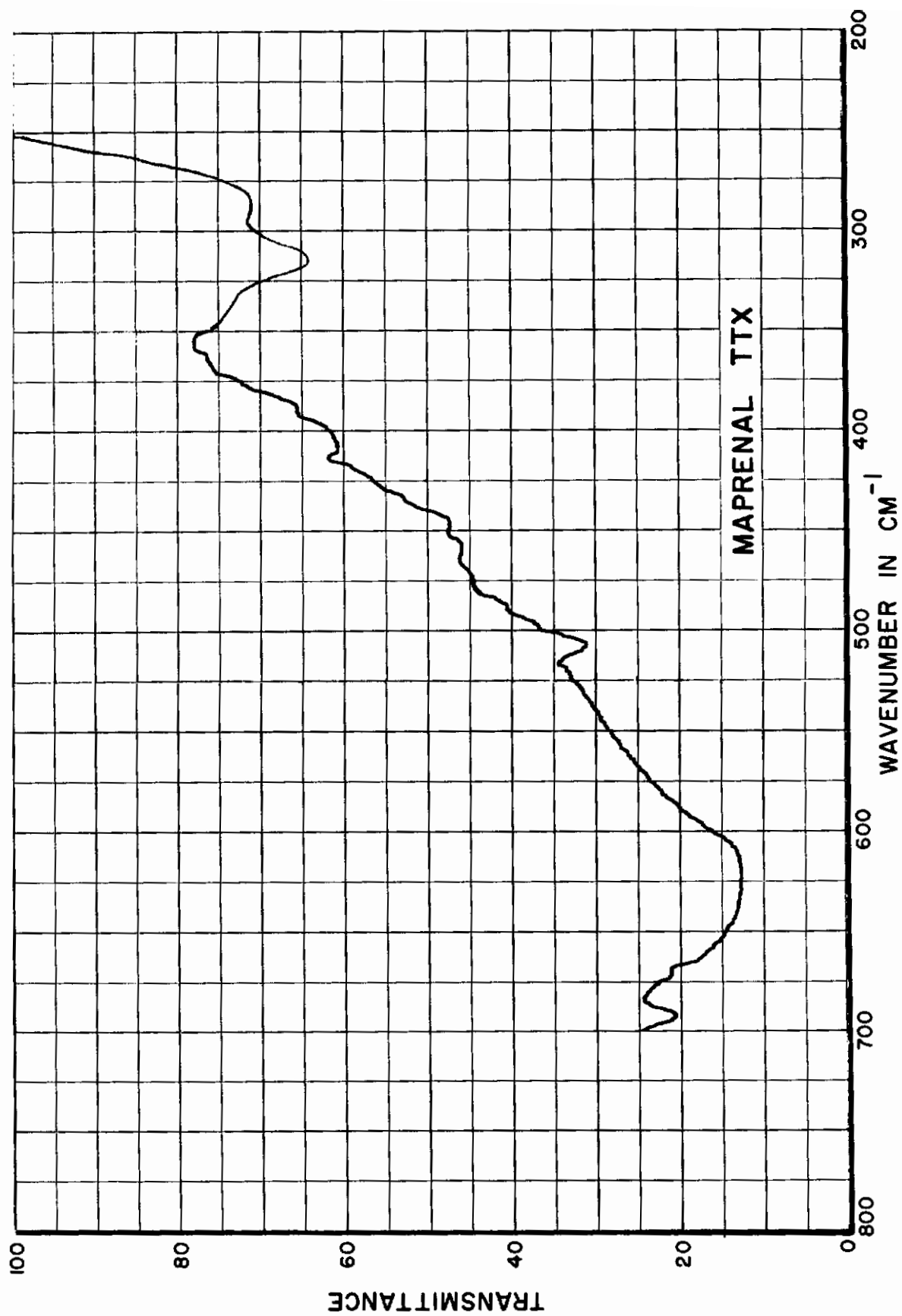


Figure 111. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Maprenal TTX (Melamine-Formaldehyde Resin)  
Recorded as a film

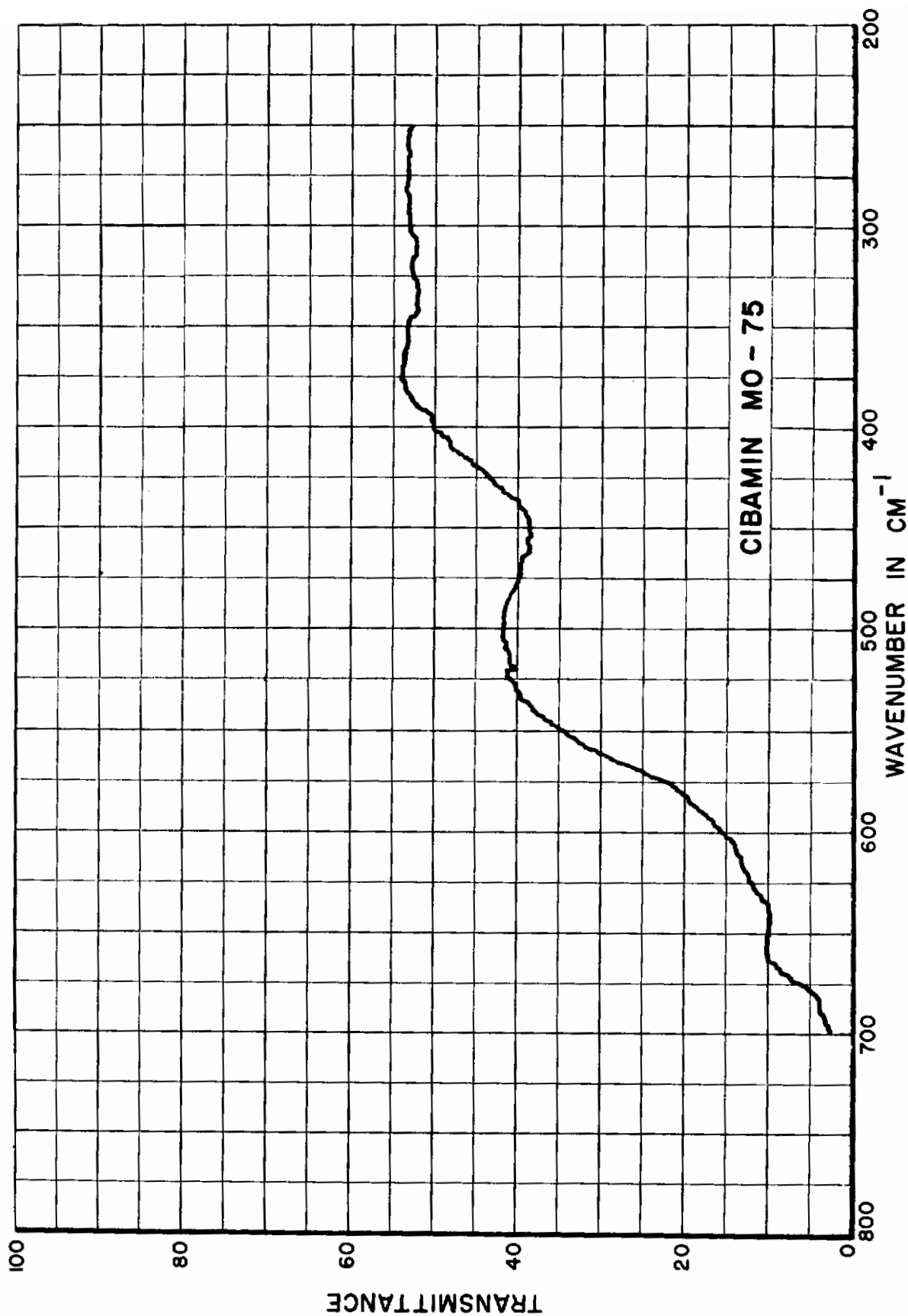


Figure 112. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Cibamin MO-75 (Oil-Modified Melamine Resin)  
Recorded as a film

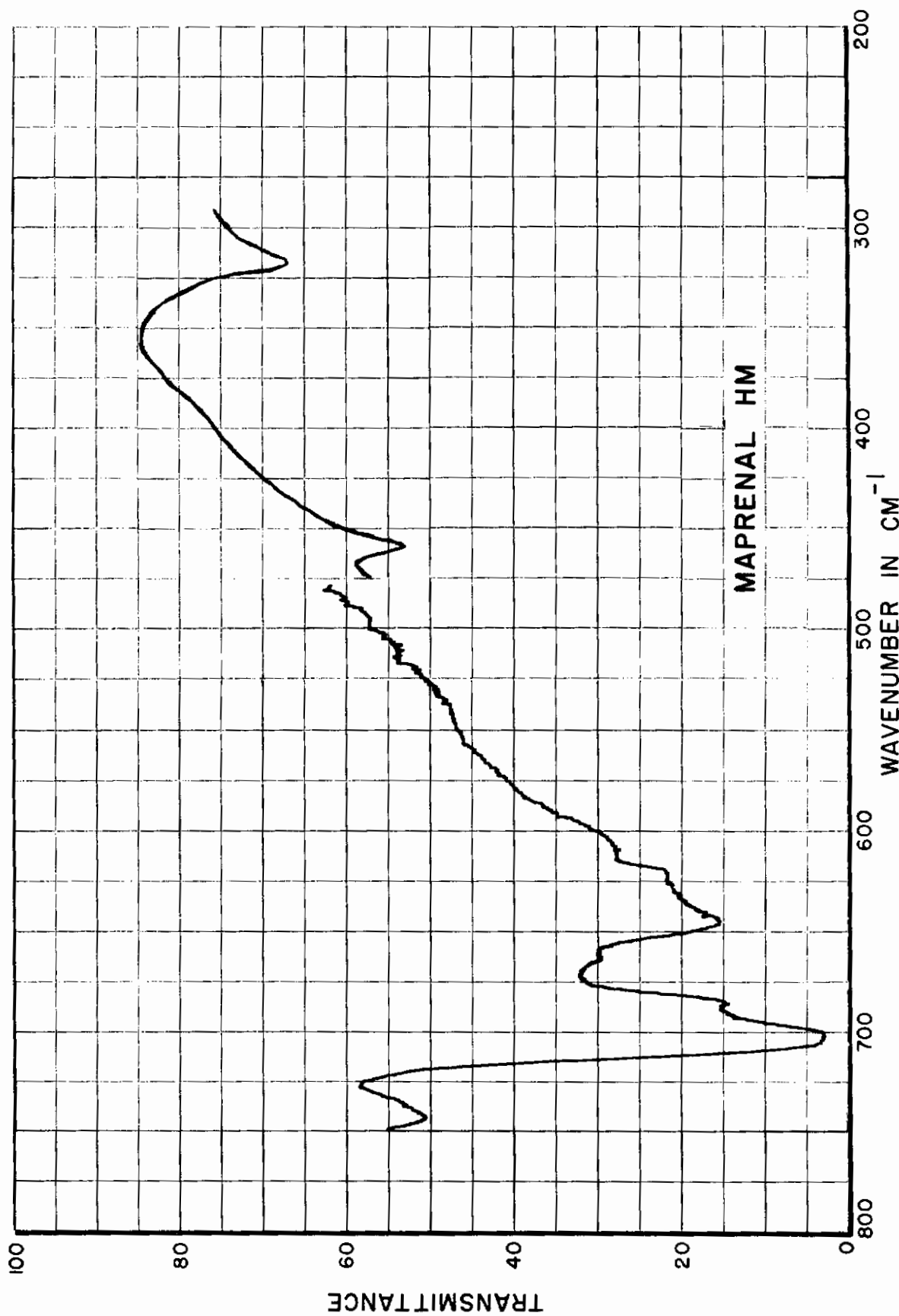


Figure 113. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Naprenal HM: (Benzoguanamine-Formaldehyde Resin)

Recorded as a film

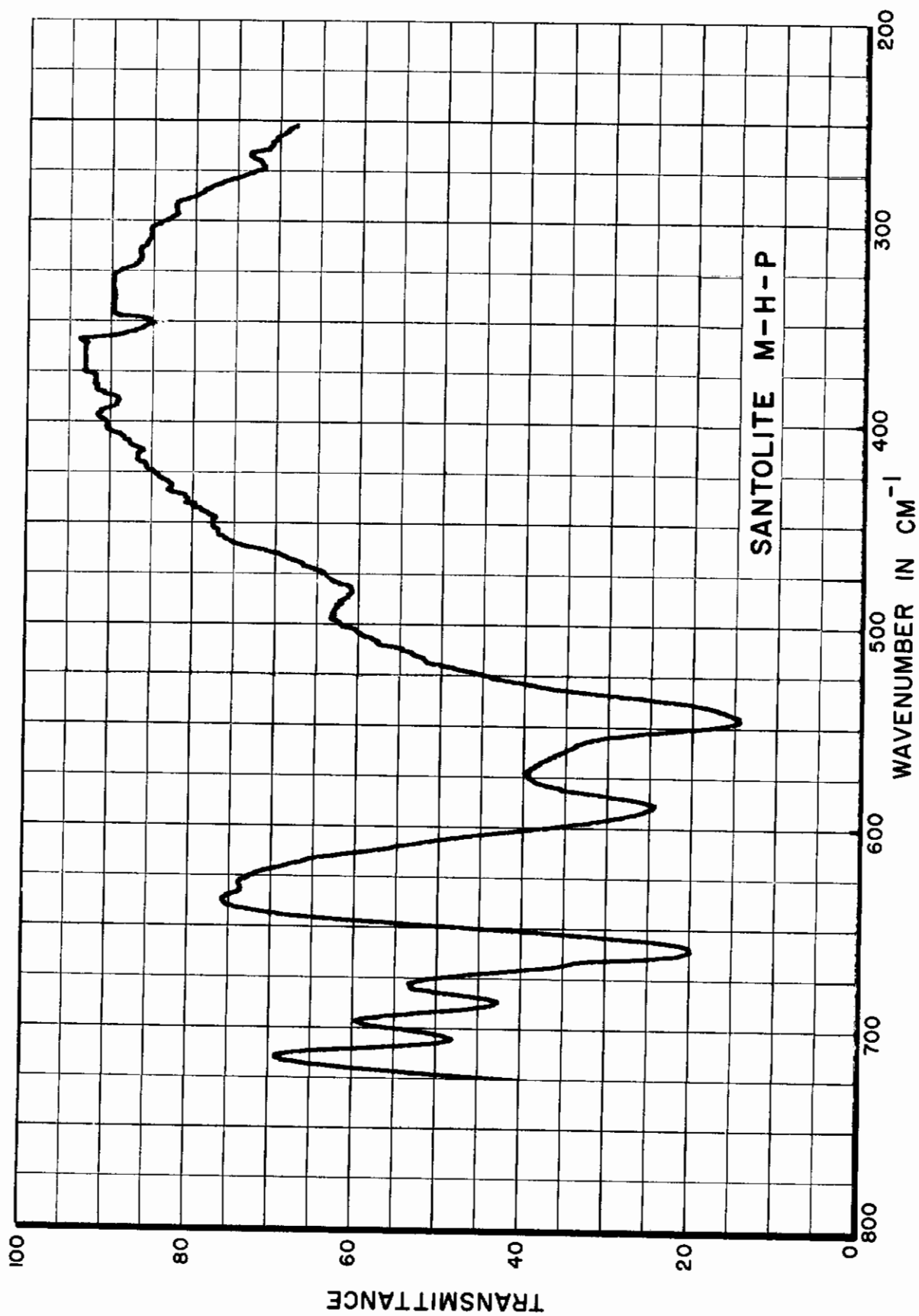


Figure 114. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Santolite N-H-P (Aromatic Sulfonamide-Formaldehyde Resin)

Recorded as a film from a chloroform solution

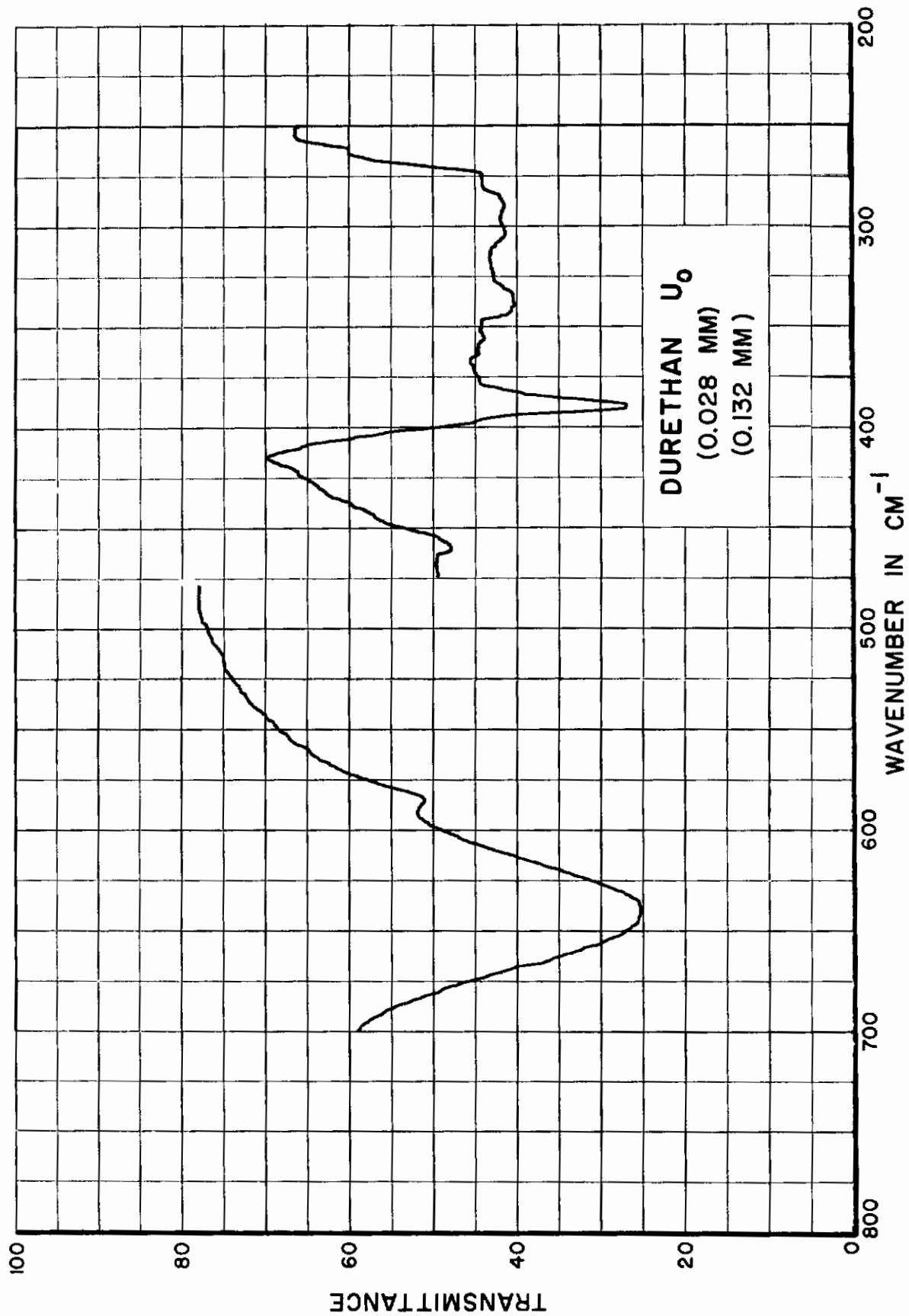


Figure 115. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Durethan U<sub>0</sub> (Polyurethane from Hexamethylene-diisocyanate and Butanediol-1,4).

Recorded as a film, prepared from a formic acid solution



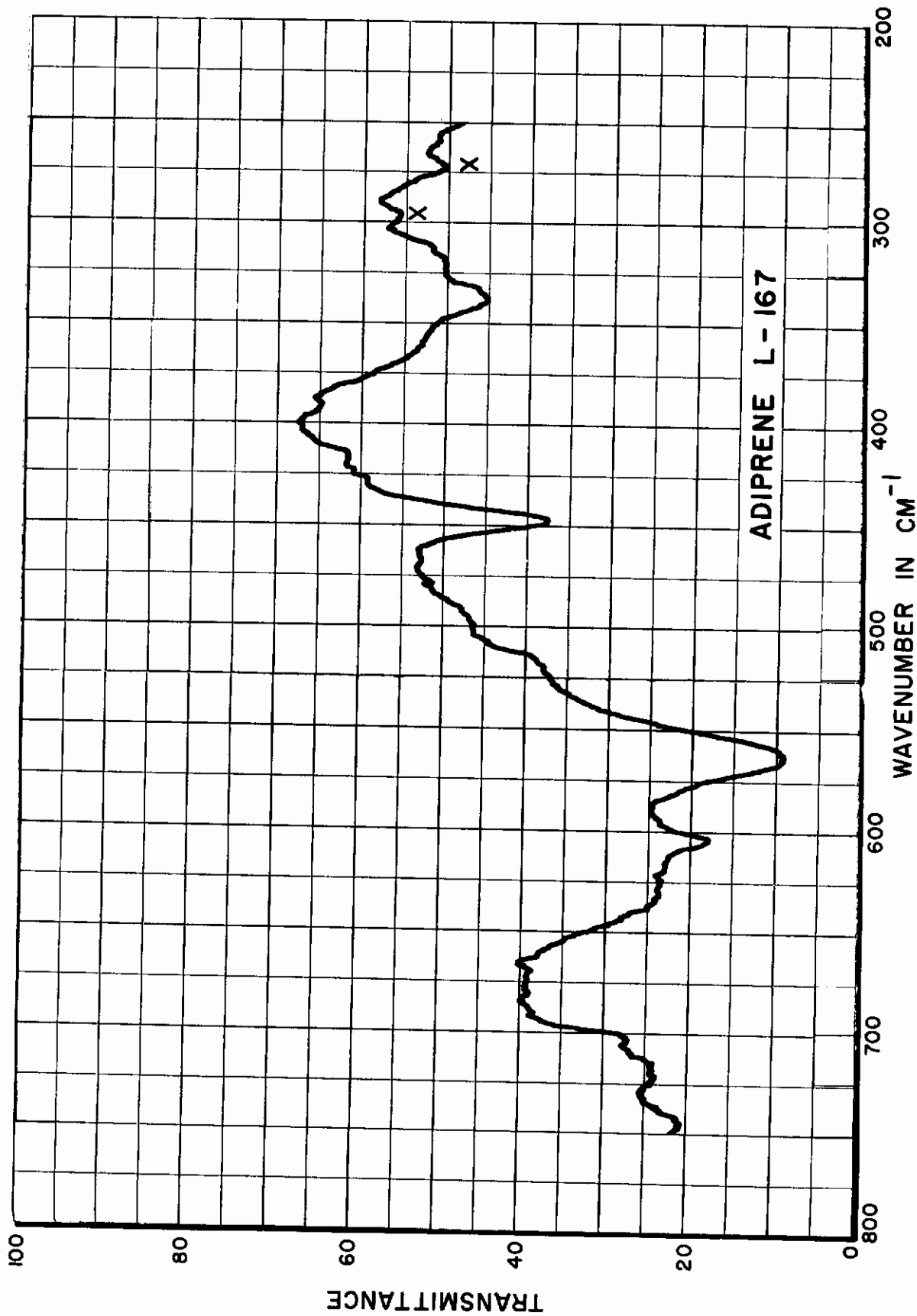


Figure 116. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Adiprene L-167 (Polyether-Alcohol Reacted with Toluene Diisocyanate)  
Recorded as a film

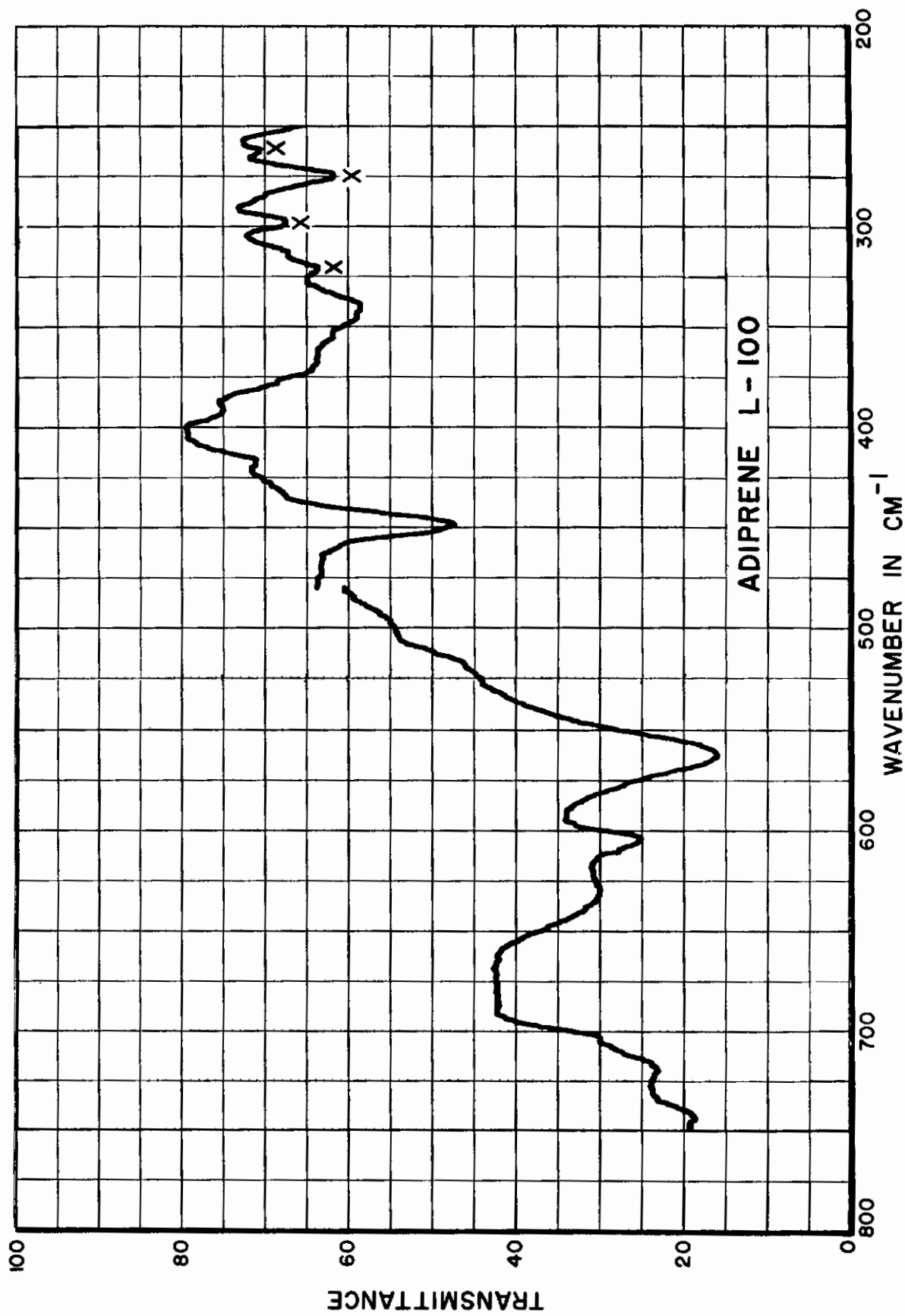


Figure 117. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Adiprene L-100 (Polyether-Alcohol Reacted with Toluene Diisocyanate)  
Recorded as a film

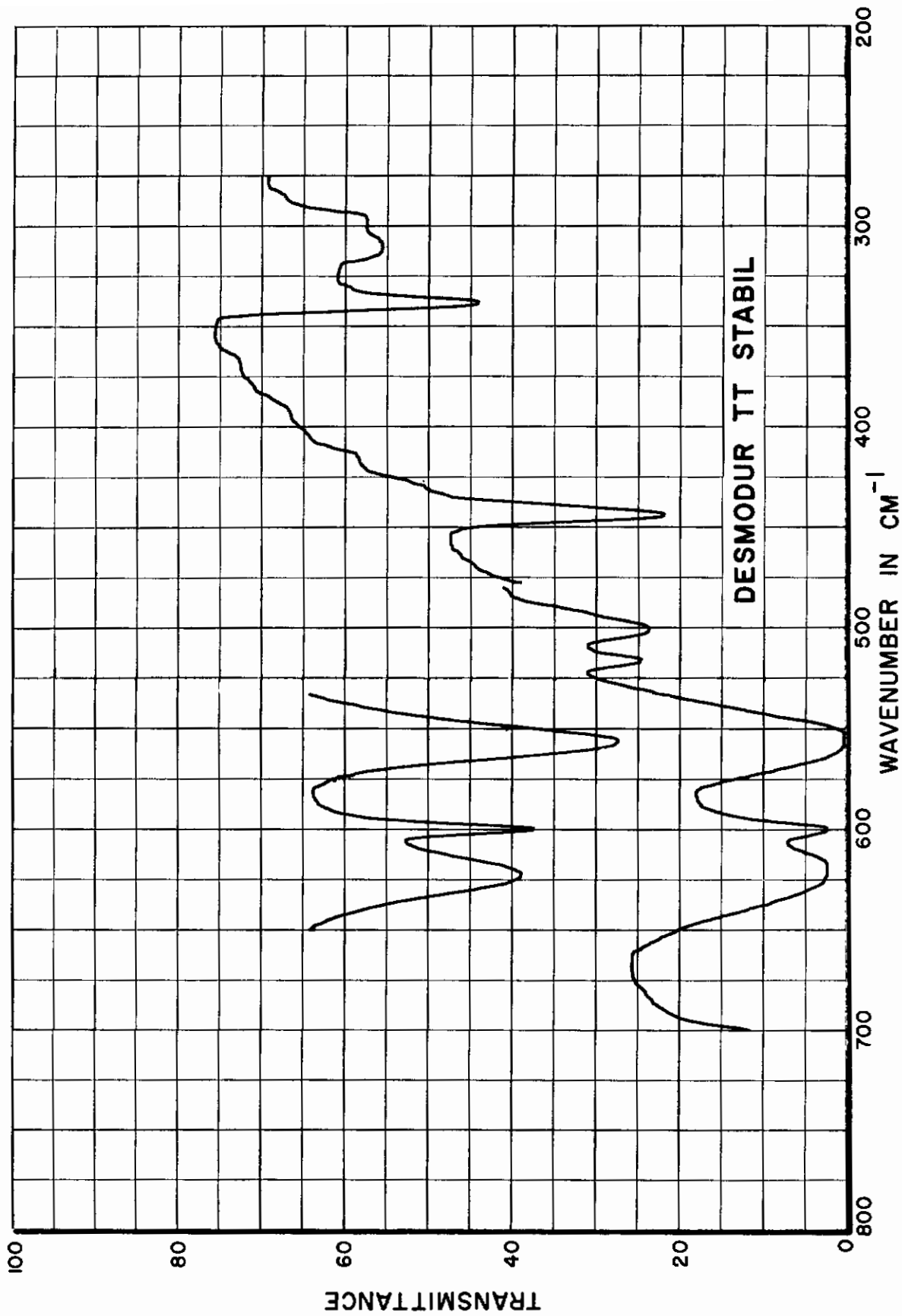


Figure 118. - Infrared Spectrum from 700 - 275 cm<sup>-1</sup> of Desmondur TT Stabil (Masked Isocyanate from Dimerized Toluene Diisocyanate and Phenol)

Recorded as a film, prepared from a chloroform solution

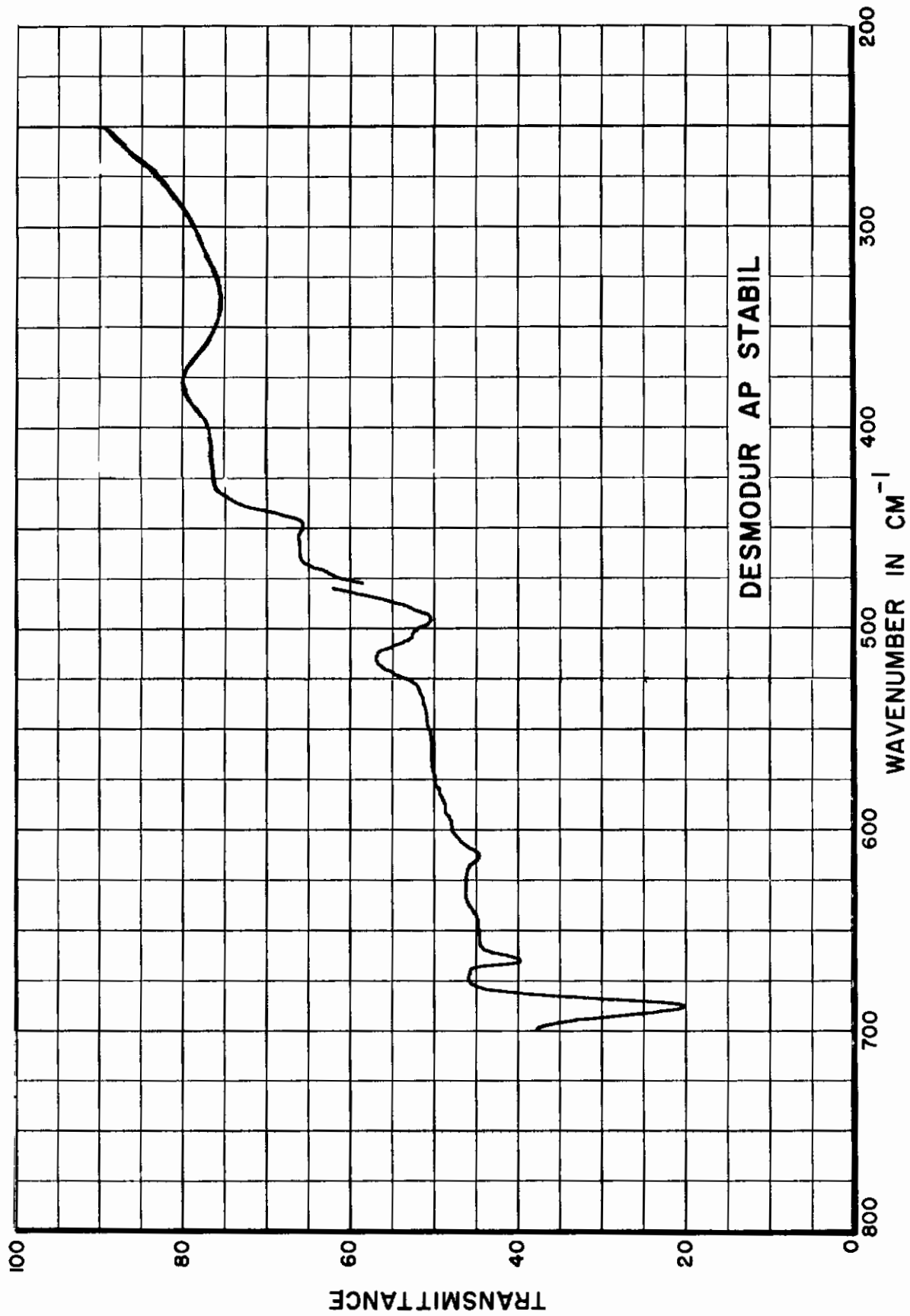


Figure 119. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Desmondur AP Stabil (Masked Isocyanate from Toluene Diisocyanate and Phenol)

Recorded as a film, prepared from a chloroform solution  
The band at 665 cm<sup>-1</sup> is due to chloroform

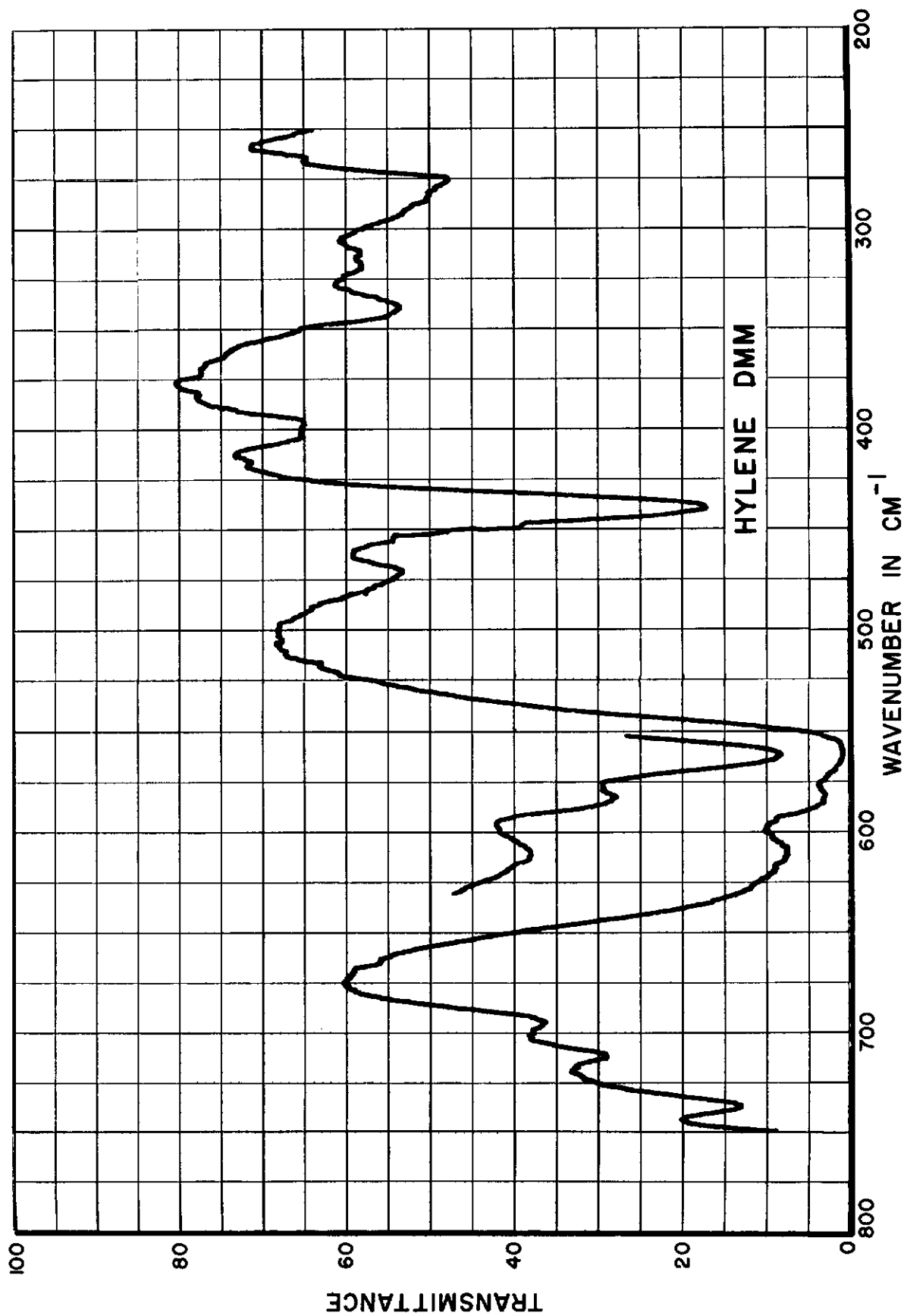


Figure 120. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Hylene DMM (4,4'-Methylene Di-o-tolylisocyanate)

Recorded as a film

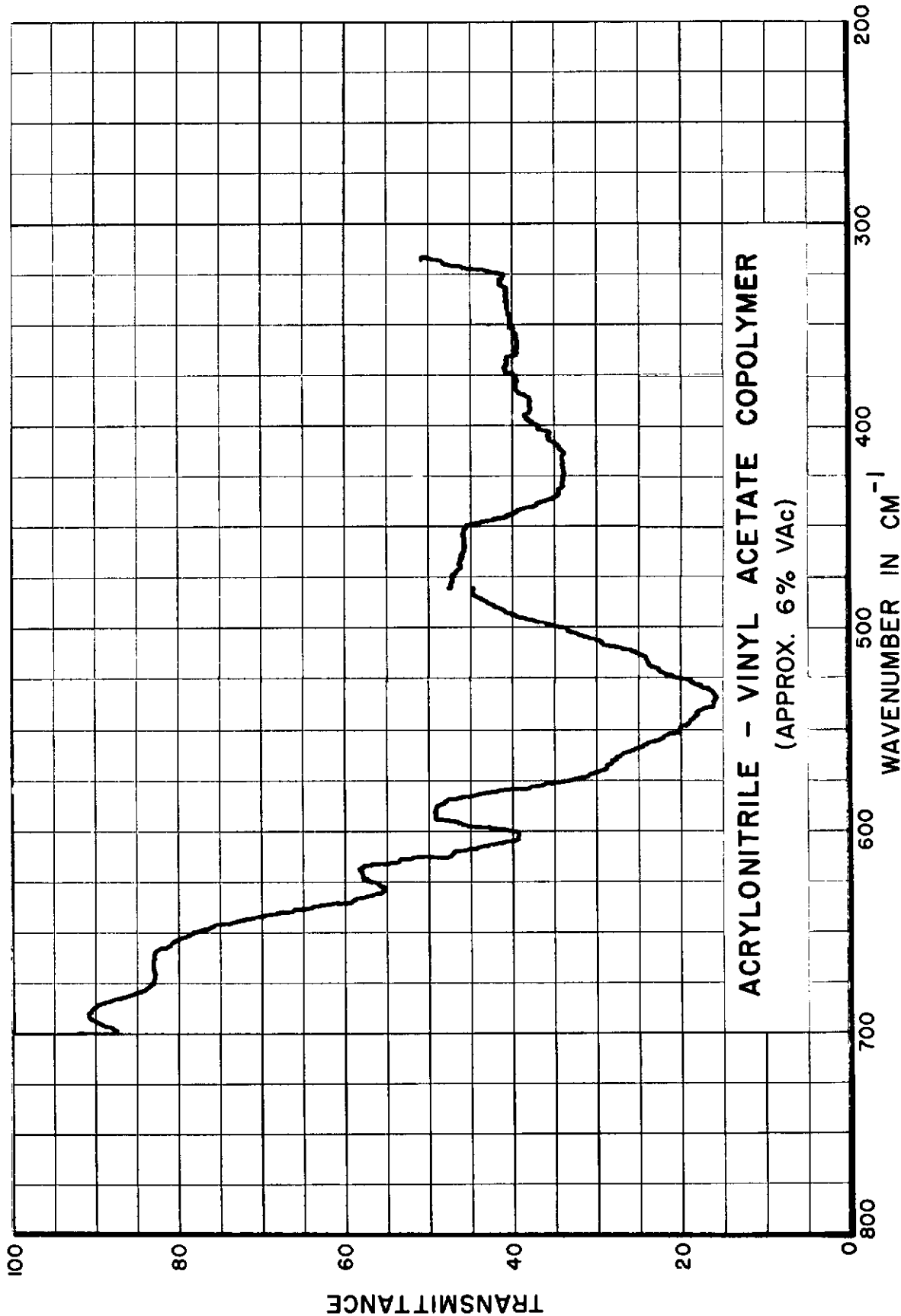


Figure 121. - Infrared Spectrum from 700 - 325  $\text{cm}^{-1}$  of a Copolymer of Acrylonitrile with 6% Vinyl Acetate  
Recorded as a Nujol mull

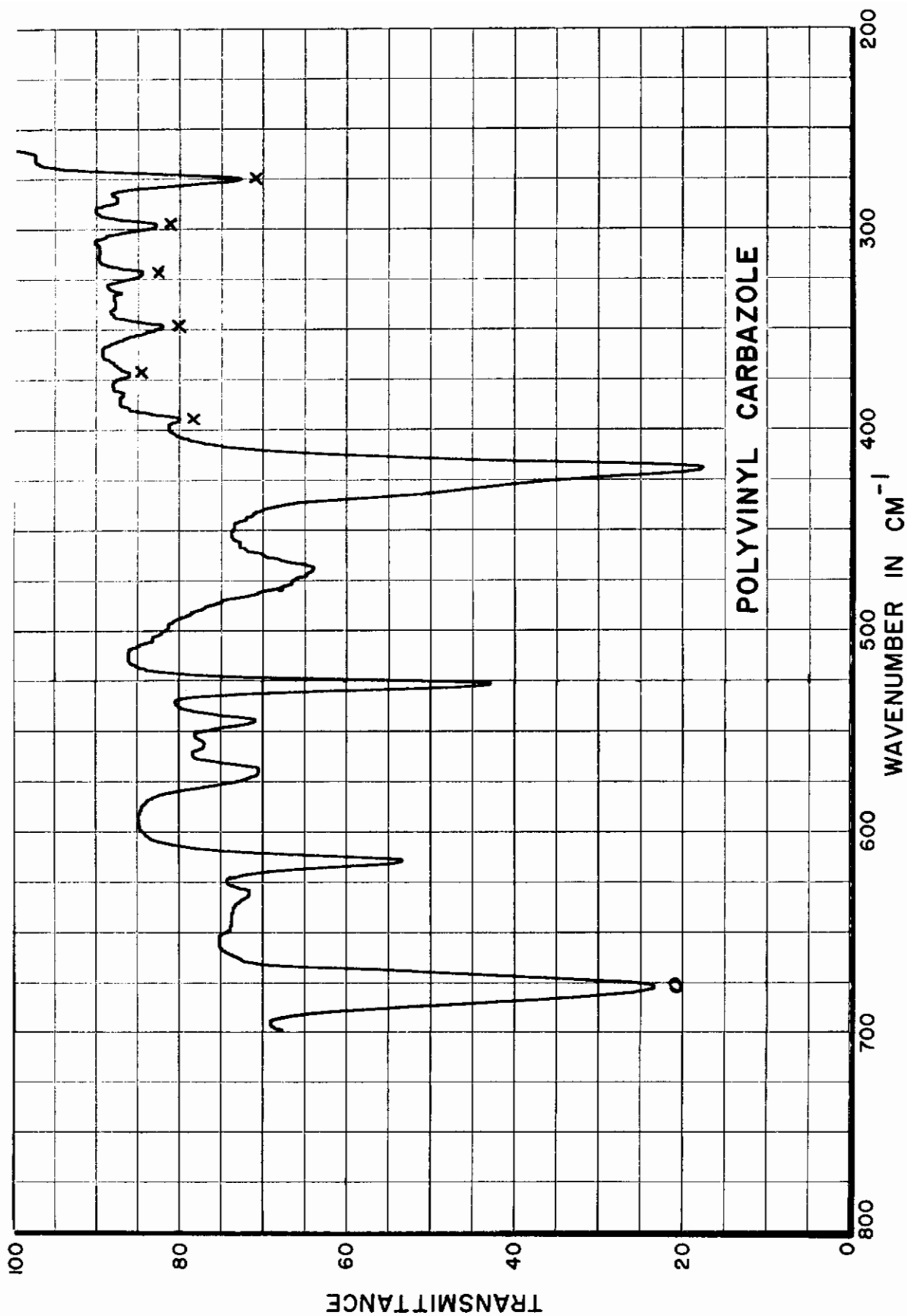


Figure 122. - Infrared Spectrum from 700 - 275 cm<sup>-1</sup> of Polyvinyl Carbazole (Luvican M 170) Recorded as a film, prepared from chloroform

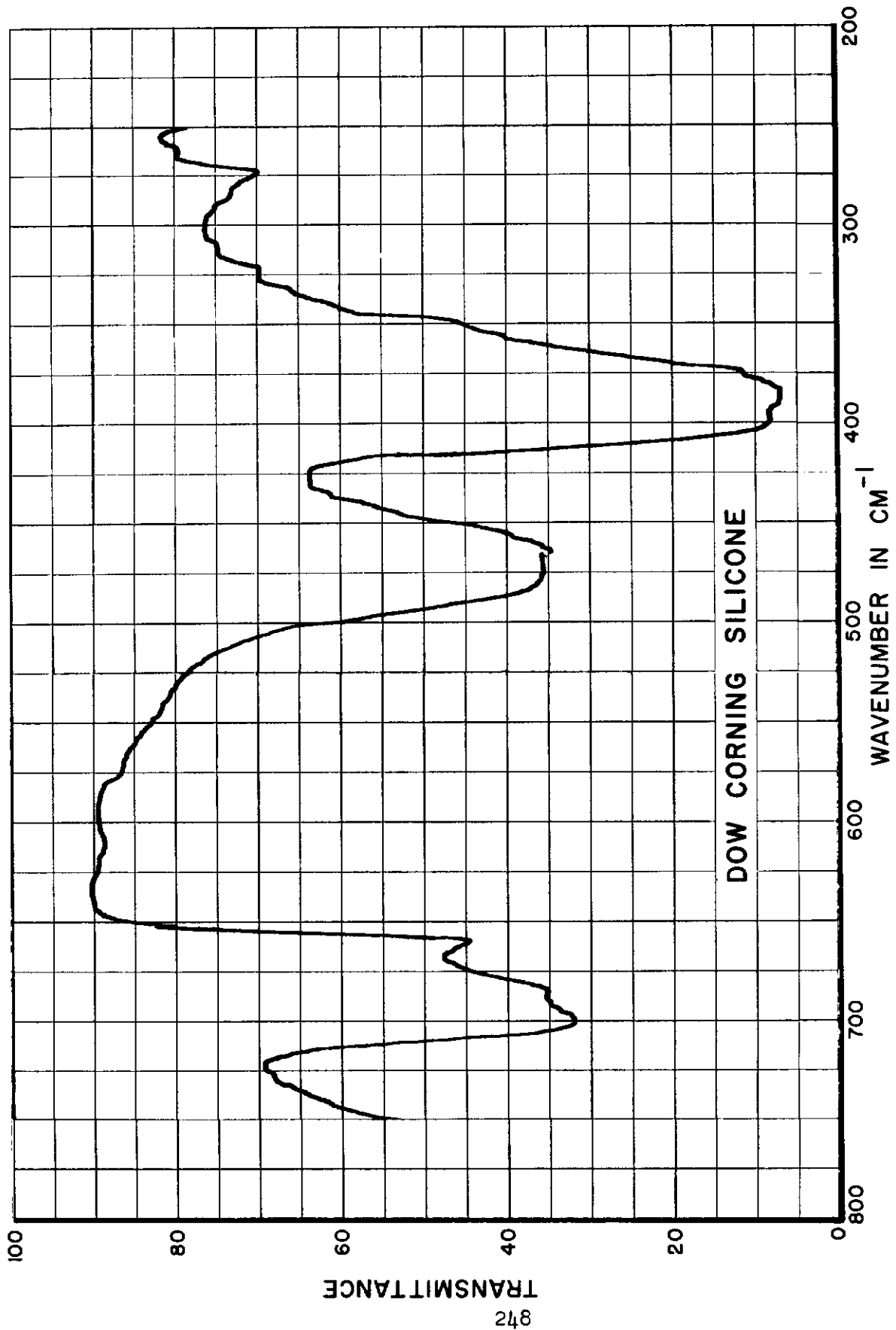


Figure 123. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Dow Corning Silicone (Polydimethylsiloxane)  
Recorded as a film 0.006 mm in thickness



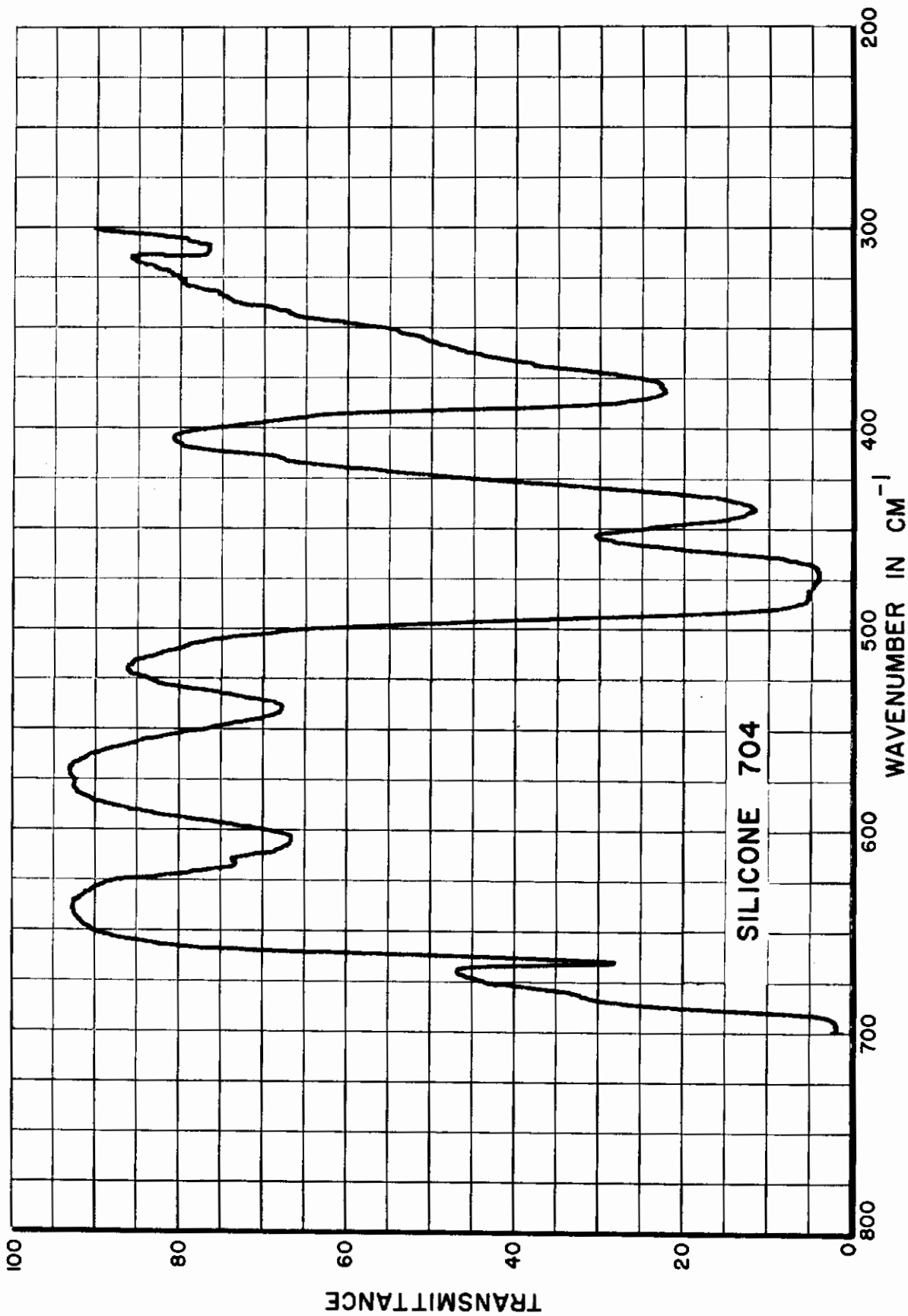


Figure 124. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Silicone 704 (Polymethylphenylsiloxane)  
Recorded as a film

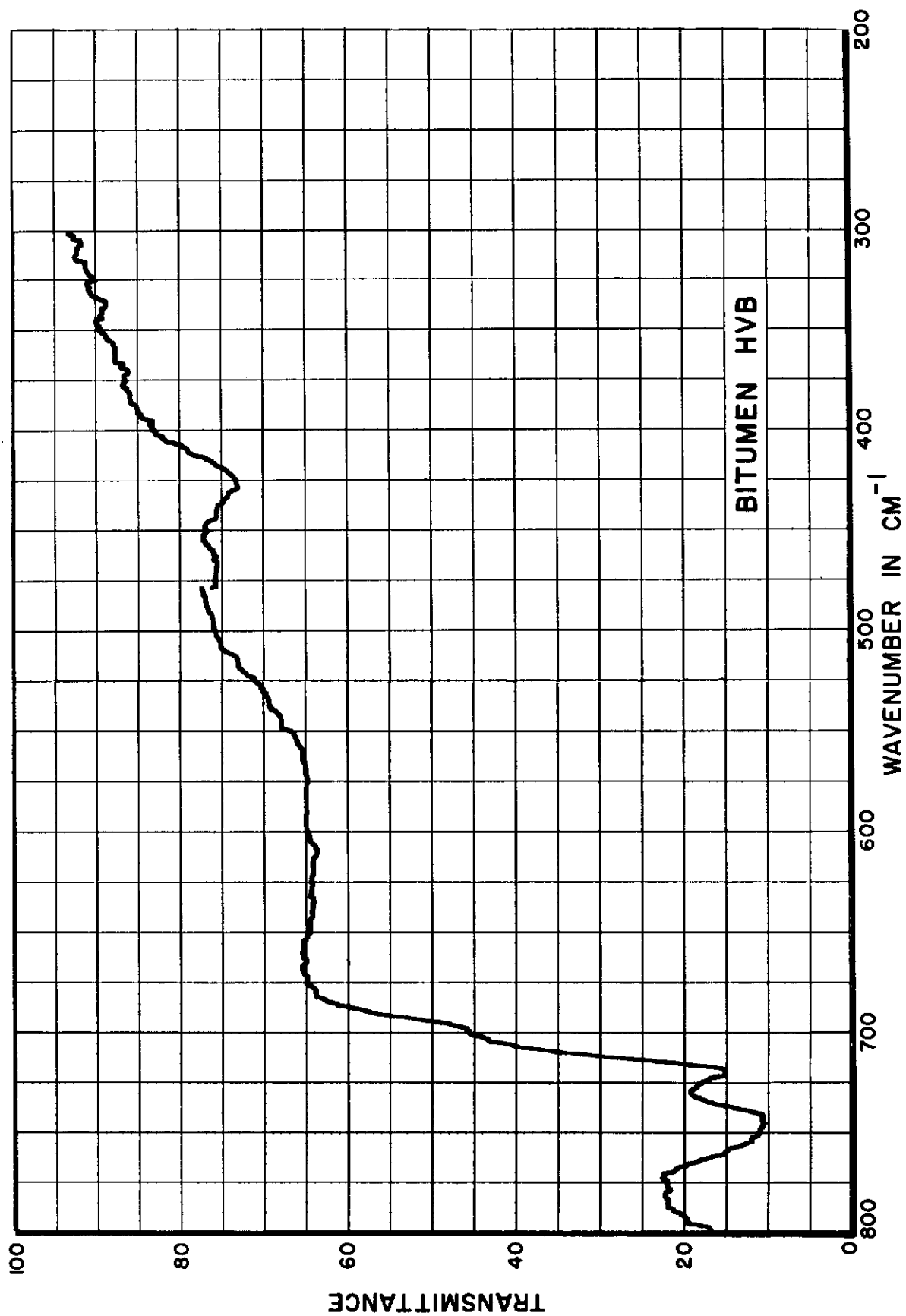


Figure 125. - Infrared Spectrum from 800 - 300  $\text{cm}^{-1}$  of Bitumen HVB (Higher Aliphatic Hydrocarbons)  
Recorded as a film

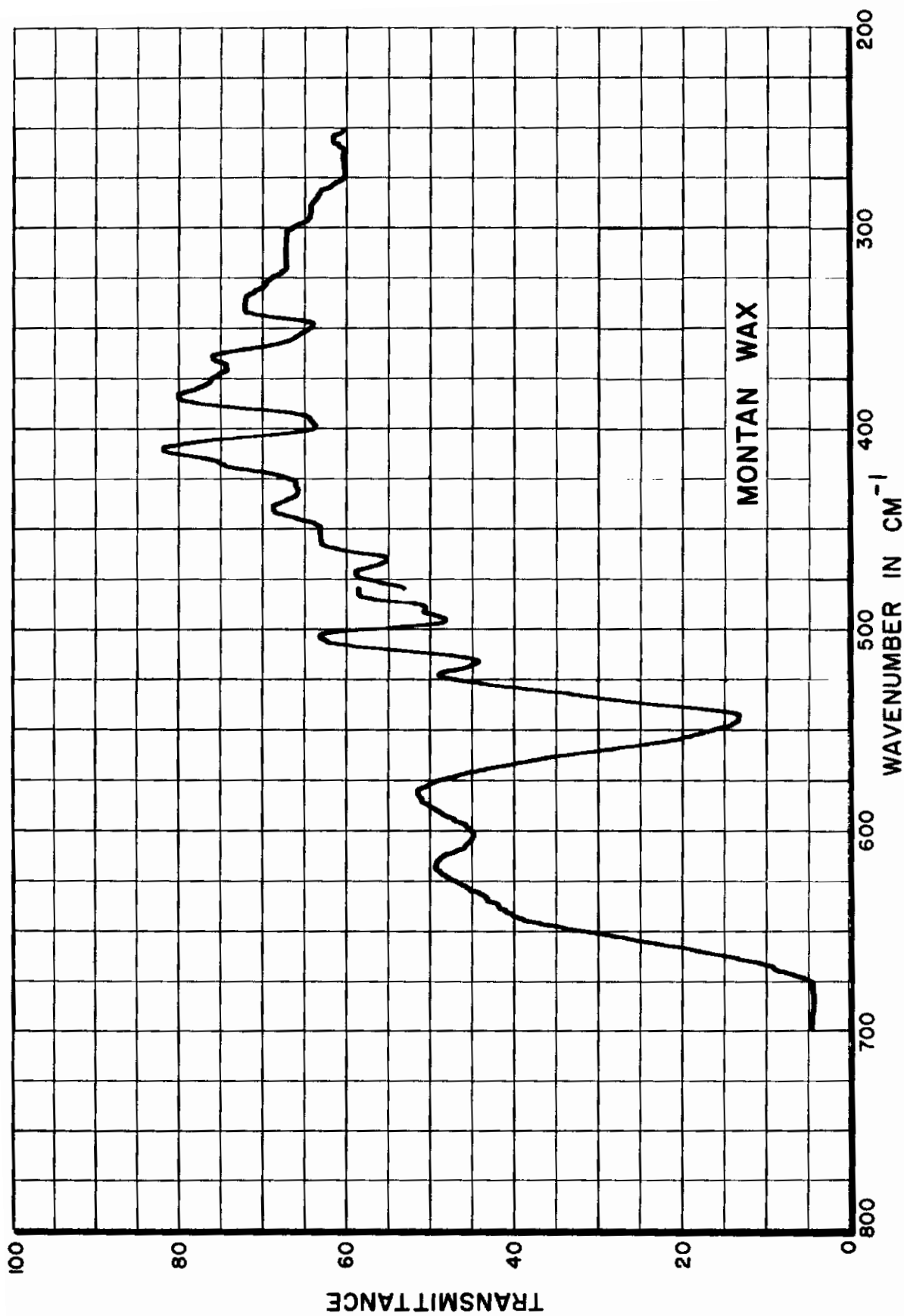


Figure 126. - Infrared Spectrum from 700 - 250  $\text{cm}^{-1}$  of Montan Wax (Mixture of High Molecular Weight Fatty Acids and Esters)  
Recorded as a film 0.6 mm in thickness

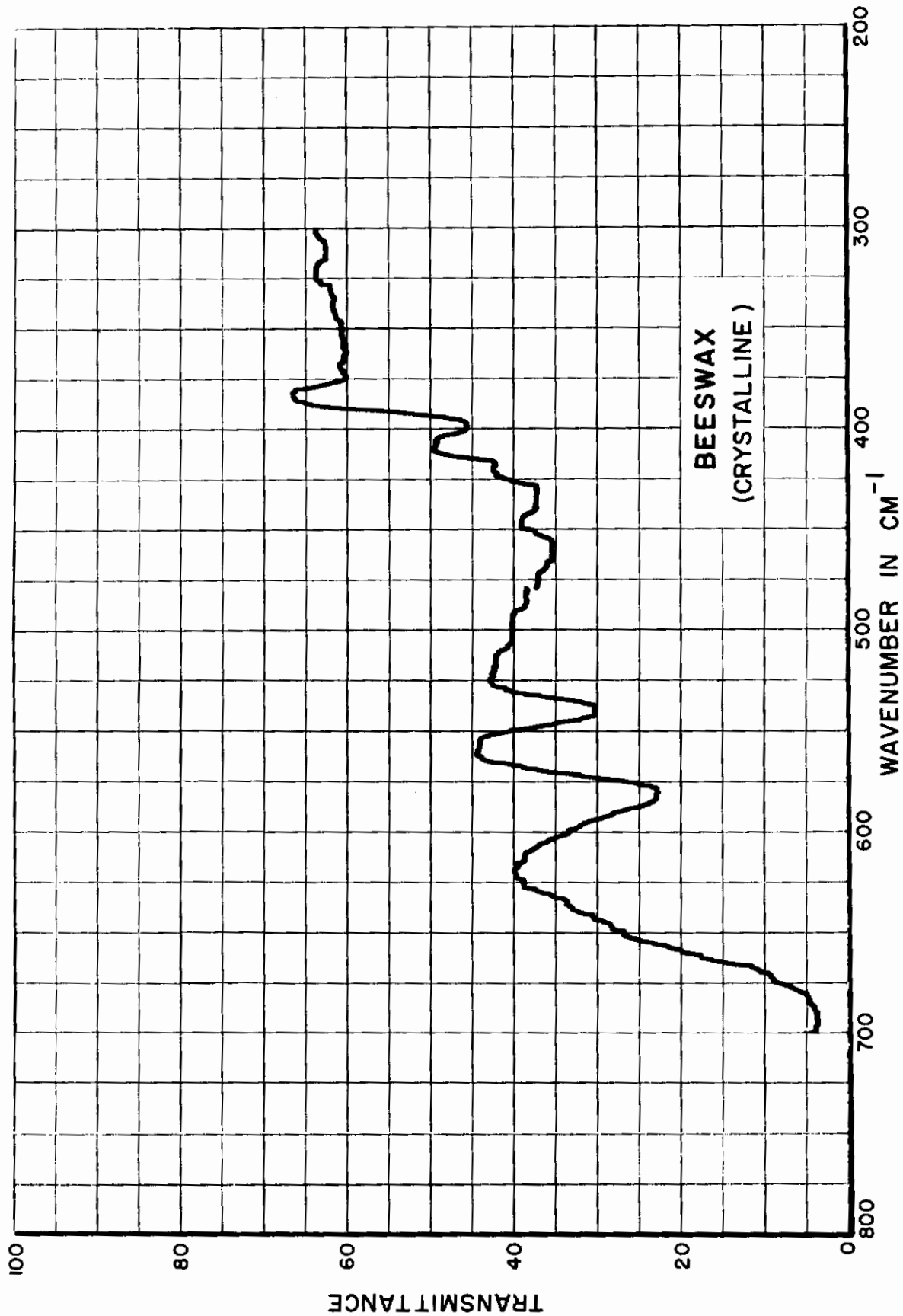


Figure 127. - Infrared Spectrum from 700 - 300  $\text{cm}^{-1}$  of Beeswax (Mixture of High Molecular Weight Esters and Fatty Acids)  
Recorded as a film

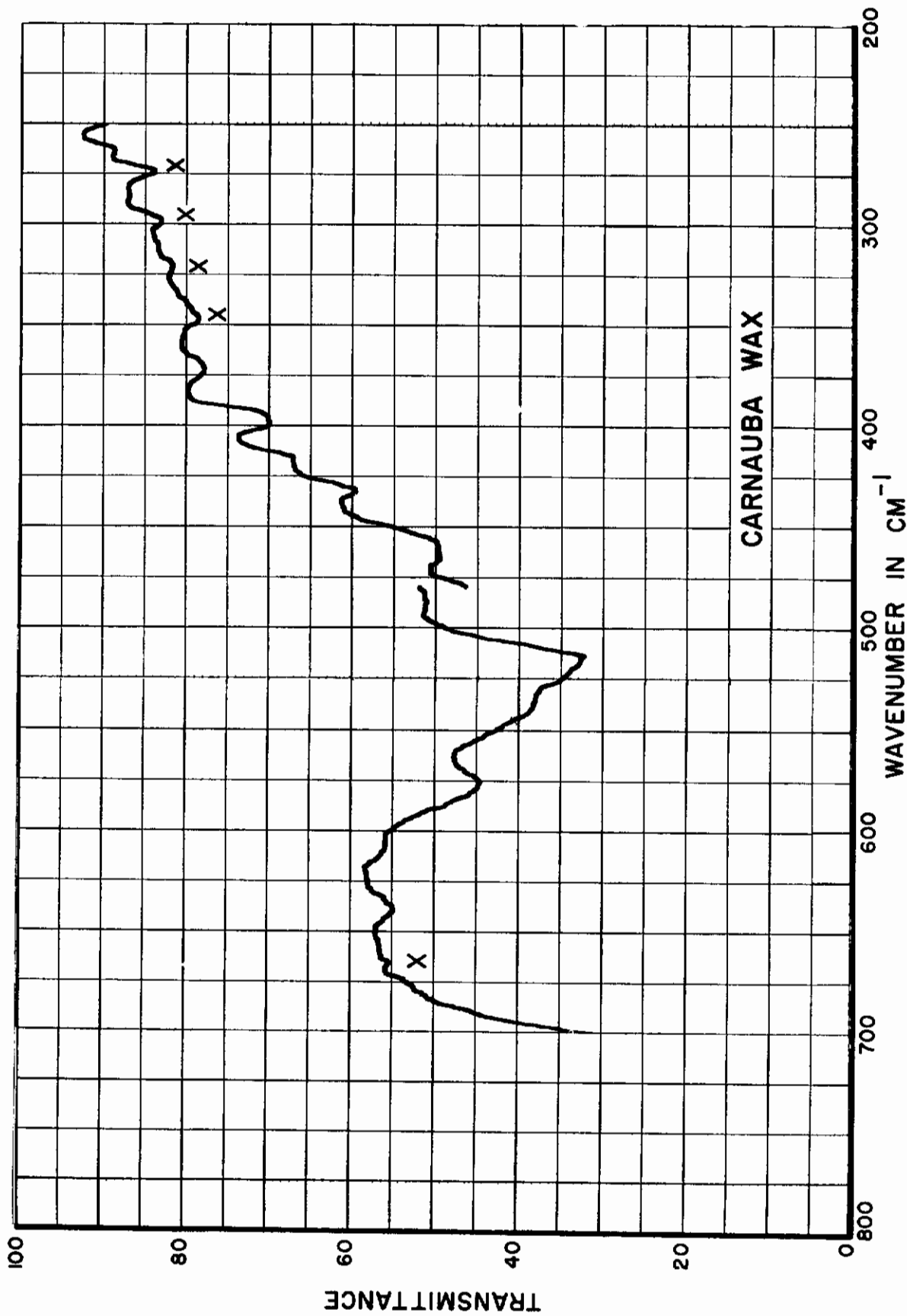


Figure 128. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Carnauba Wax (Mixture of High Molecular Weight Aliphatic Hydrocarbons, Alcohols and Esters)  
Recorded as a film approximately 0.30 mm in thickness

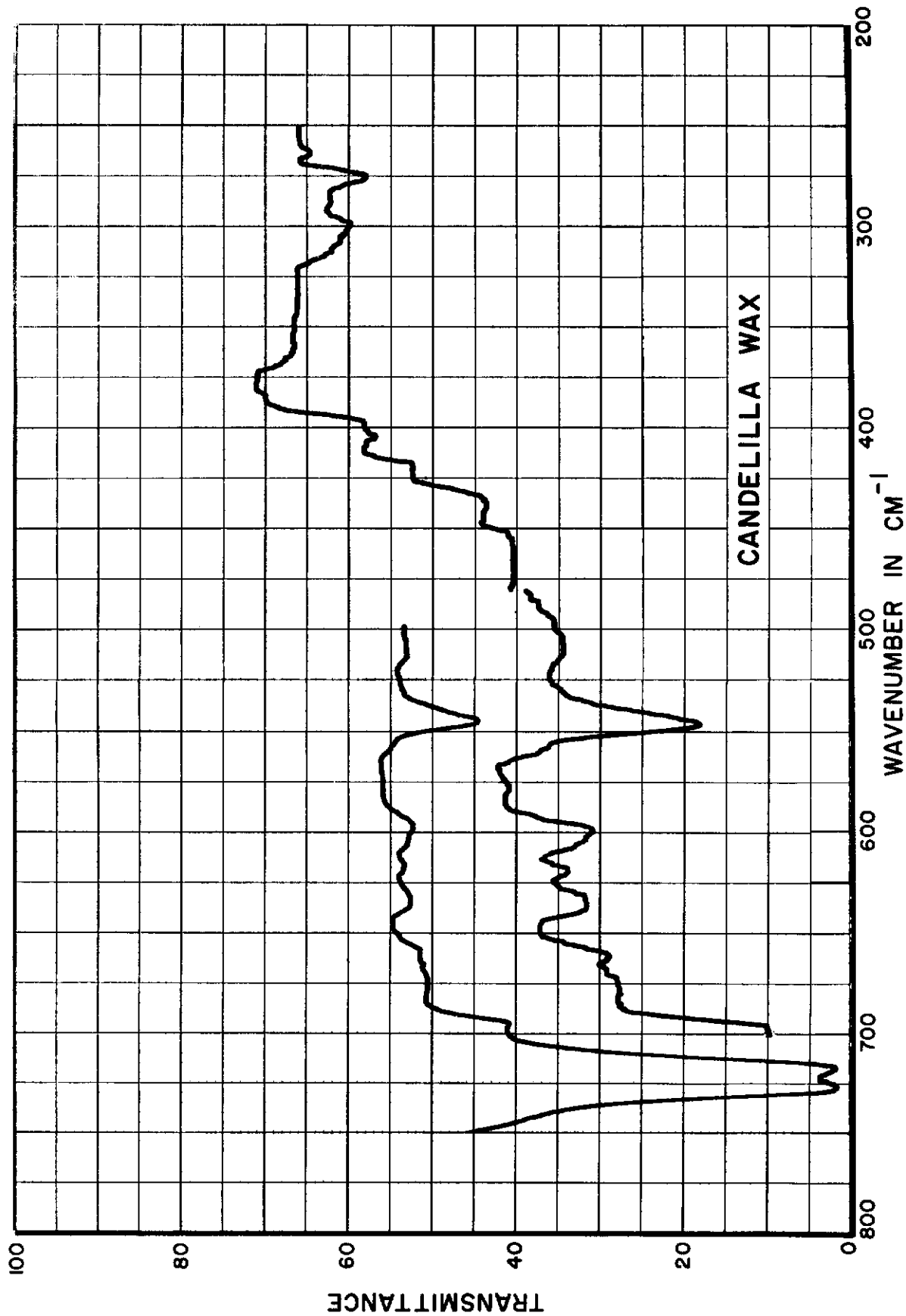


Figure 129. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Candelilla Wax (Mixture of High Molecular Weight Hydrocarbons and Ester-Type and Acid Resins)  
Recorded as a film approximately 1.5 mm in thickness

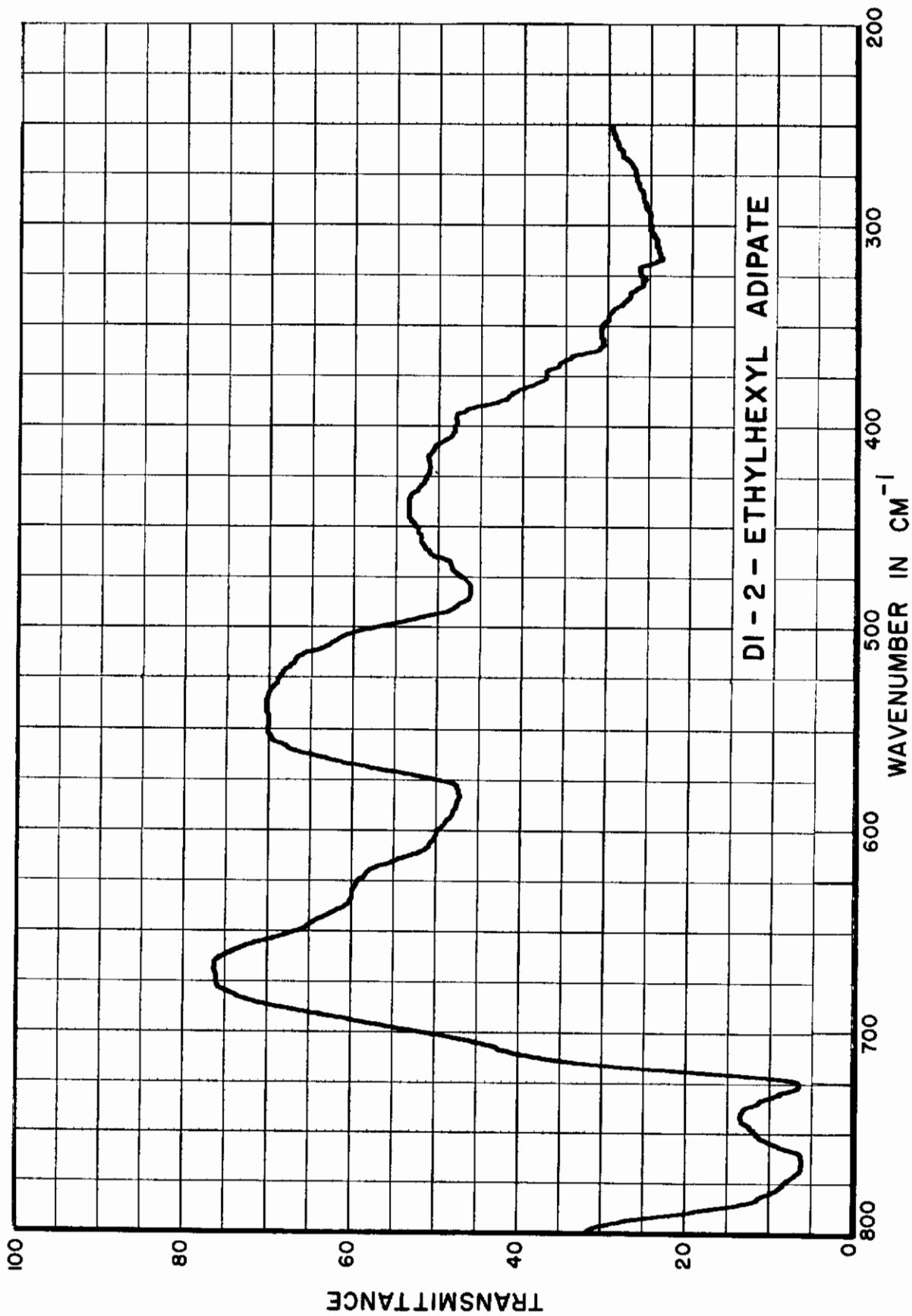


Figure 130. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Di-2-Ethylhexyl Adipate  
Recorded using a 0.21 mm CsBr cell

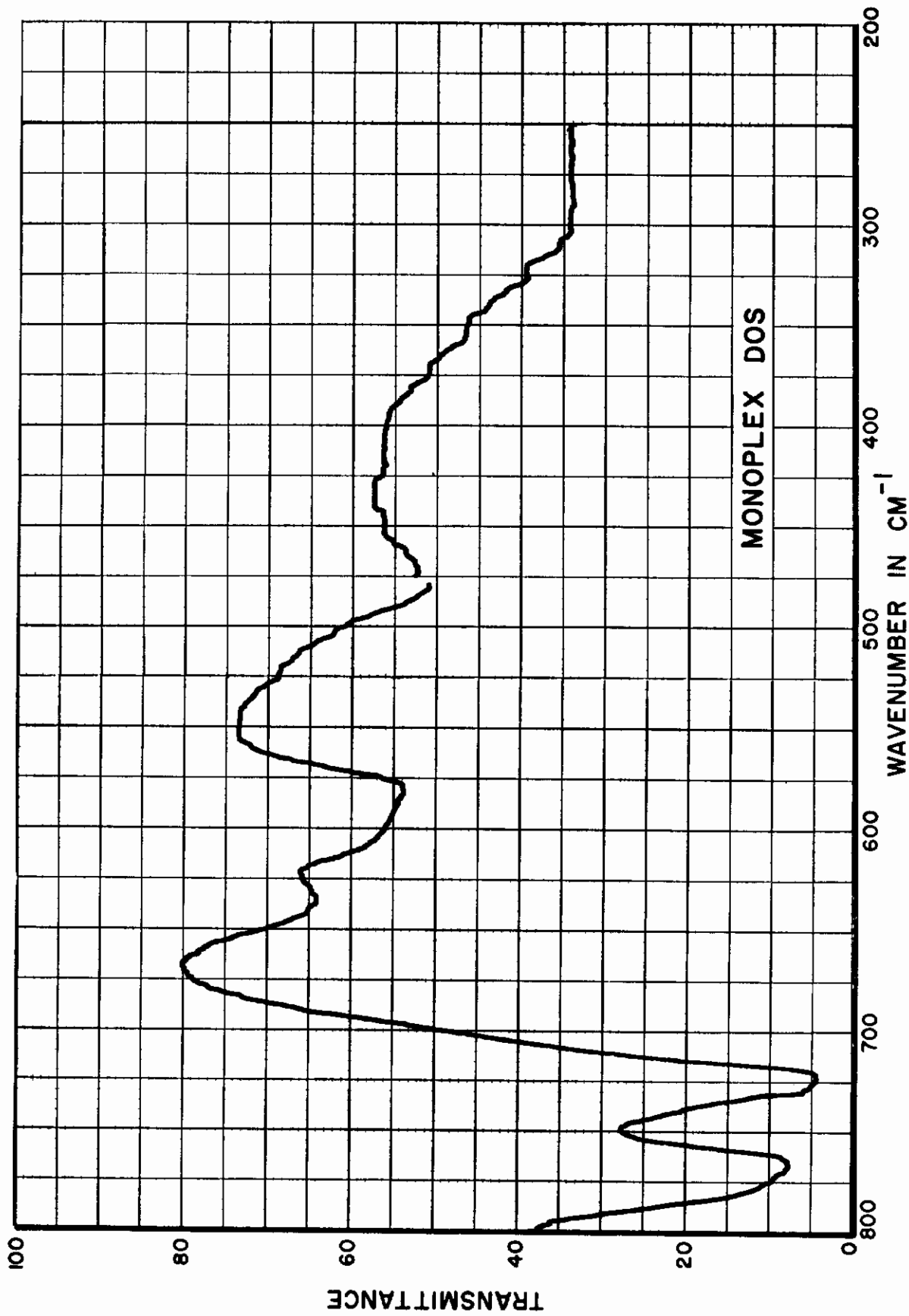


Figure 131. - Infrared Spectrum from 800 - 250 cm<sup>-1</sup> of Monoplex DOS (Di-2-Ethylhexyl Sebacate) Recorded using a 0.41 mm CsBr cell



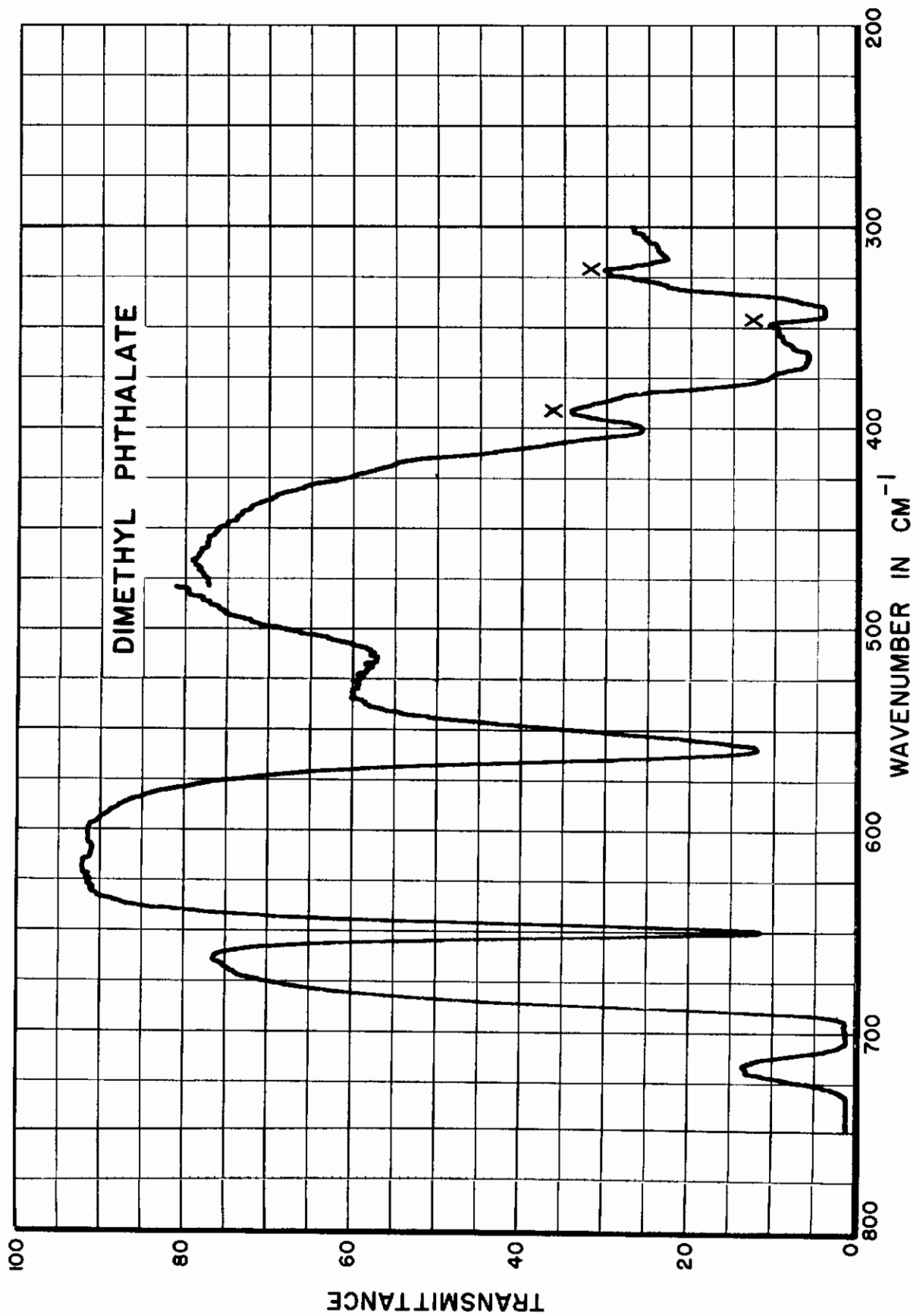


Figure 132. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Dimethyl Phthalate  
Recorded using a 0.1 mm CsBr cell

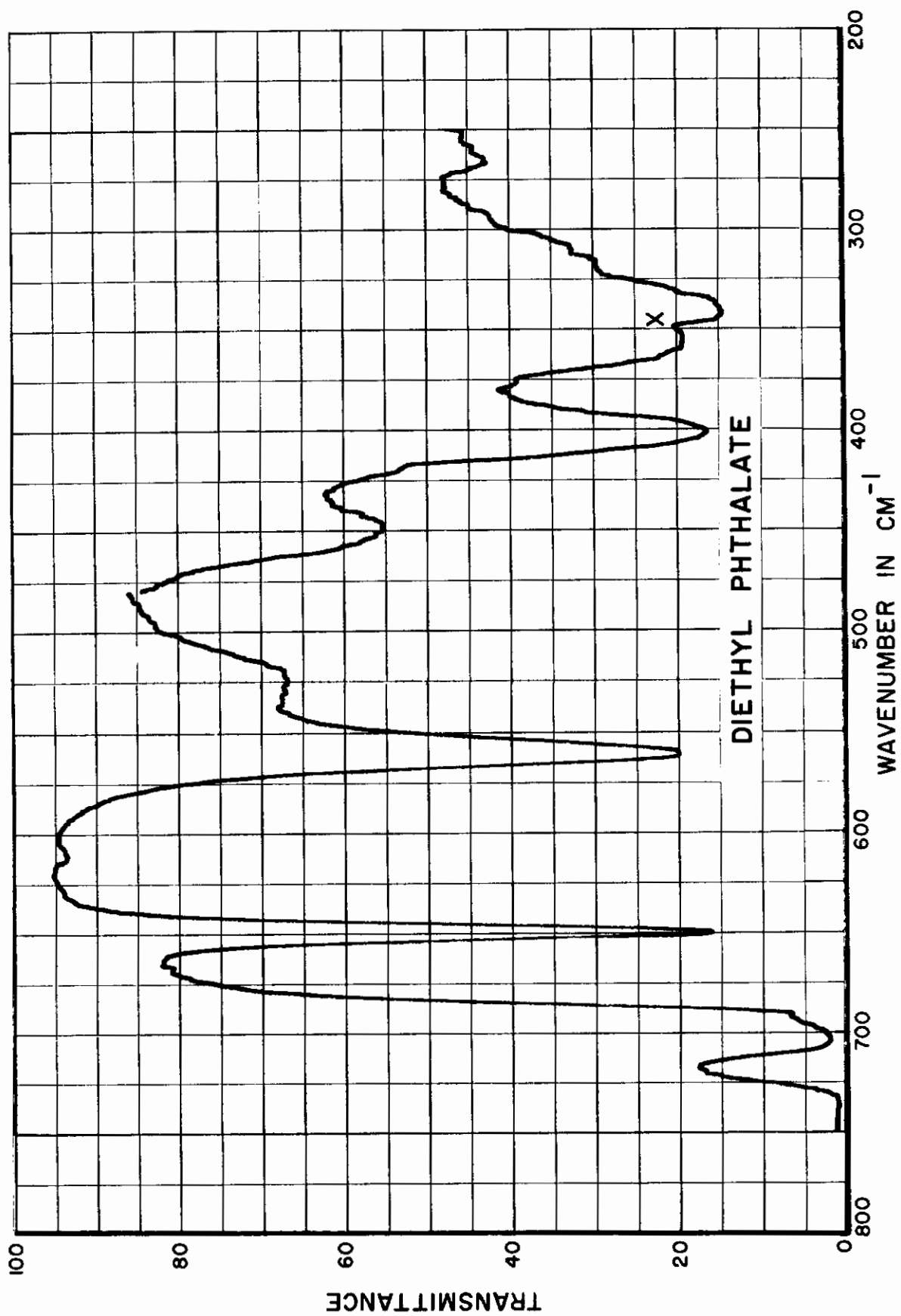


Figure 133. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Diethyl Phthalate recorded using a 0.1 mm CsBr cell

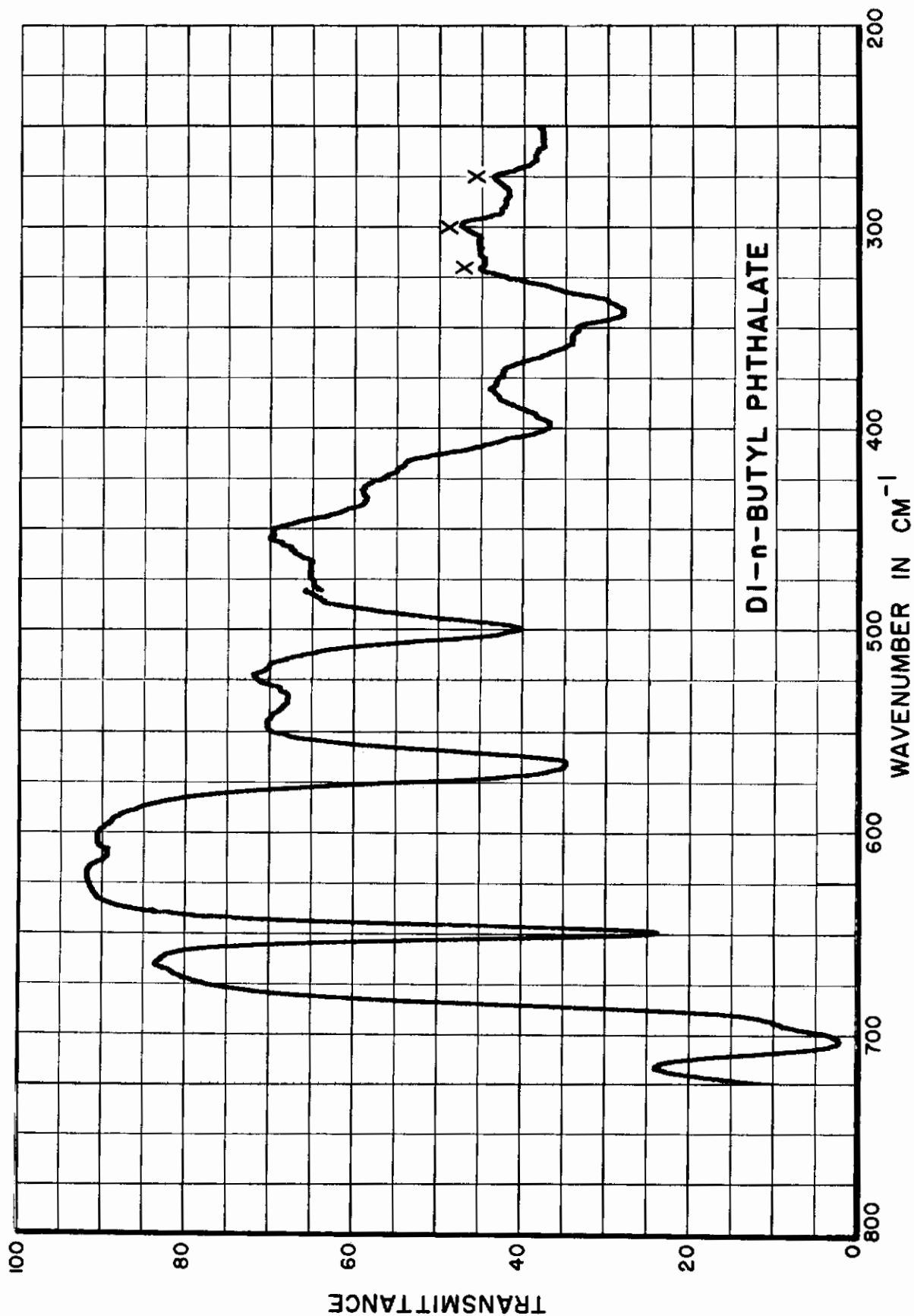


Figure 134. - Infrared Spectrum from 725 - 250  $\text{cm}^{-1}$  of Di-n-Butyl Phthalate  
Recorded using a 0.1 mm CsBr cell

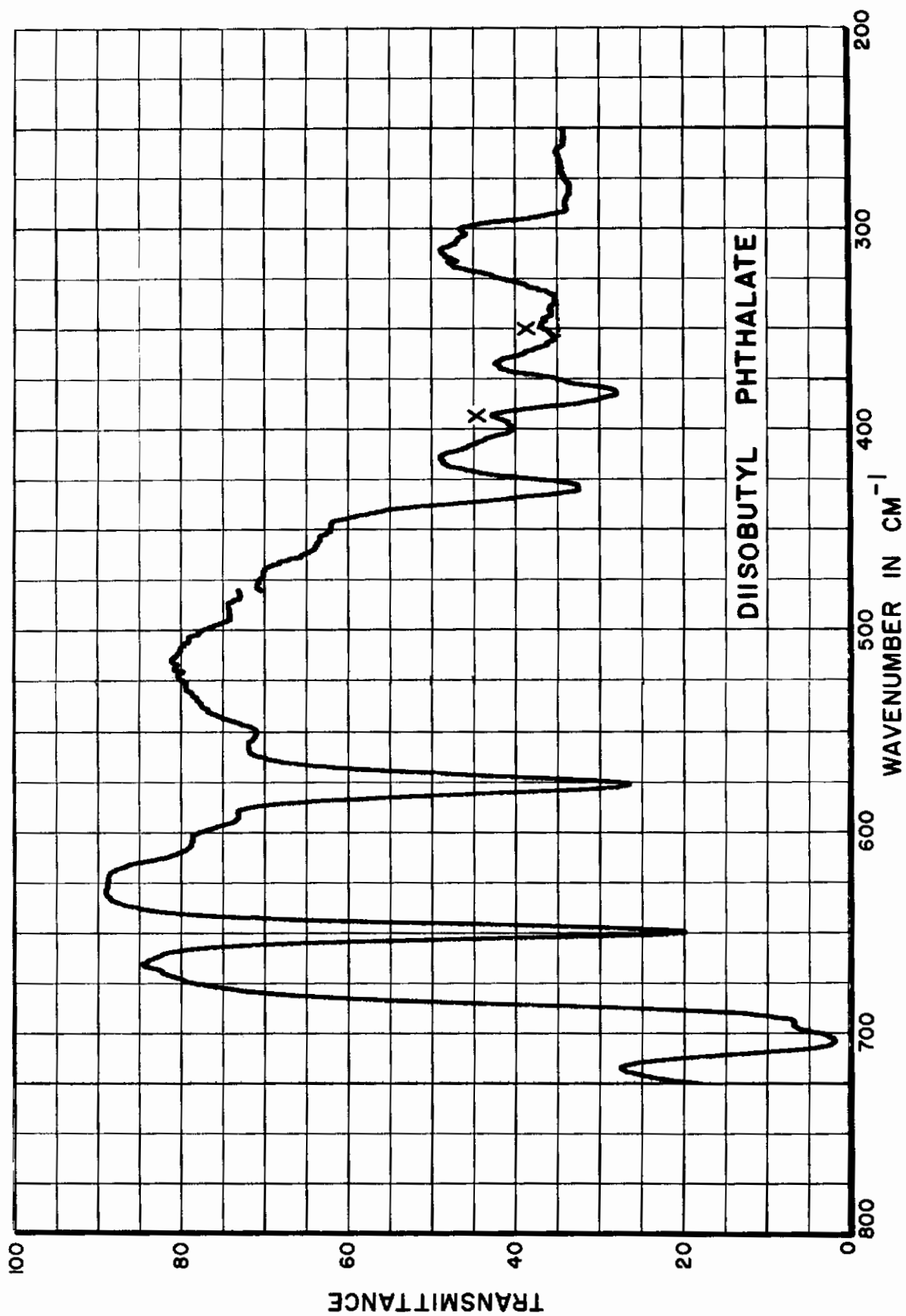


Figure 135. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Diisobutyl Phthalate  
Recorded using a 0.1 mm CsBr cell

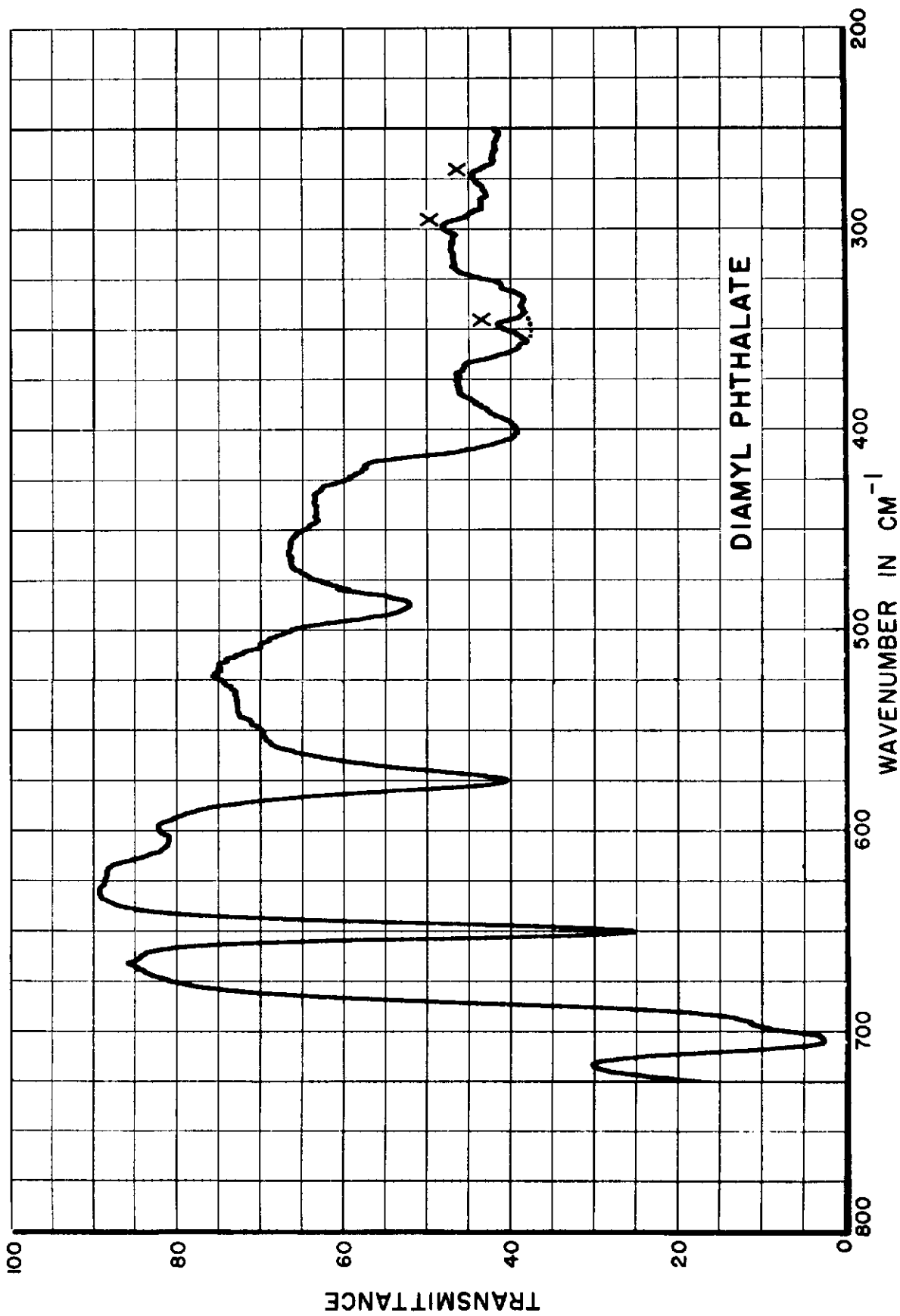


Figure 136. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Diamyl Phthalate  
Recorded using a 0.1 mm CsBr cell

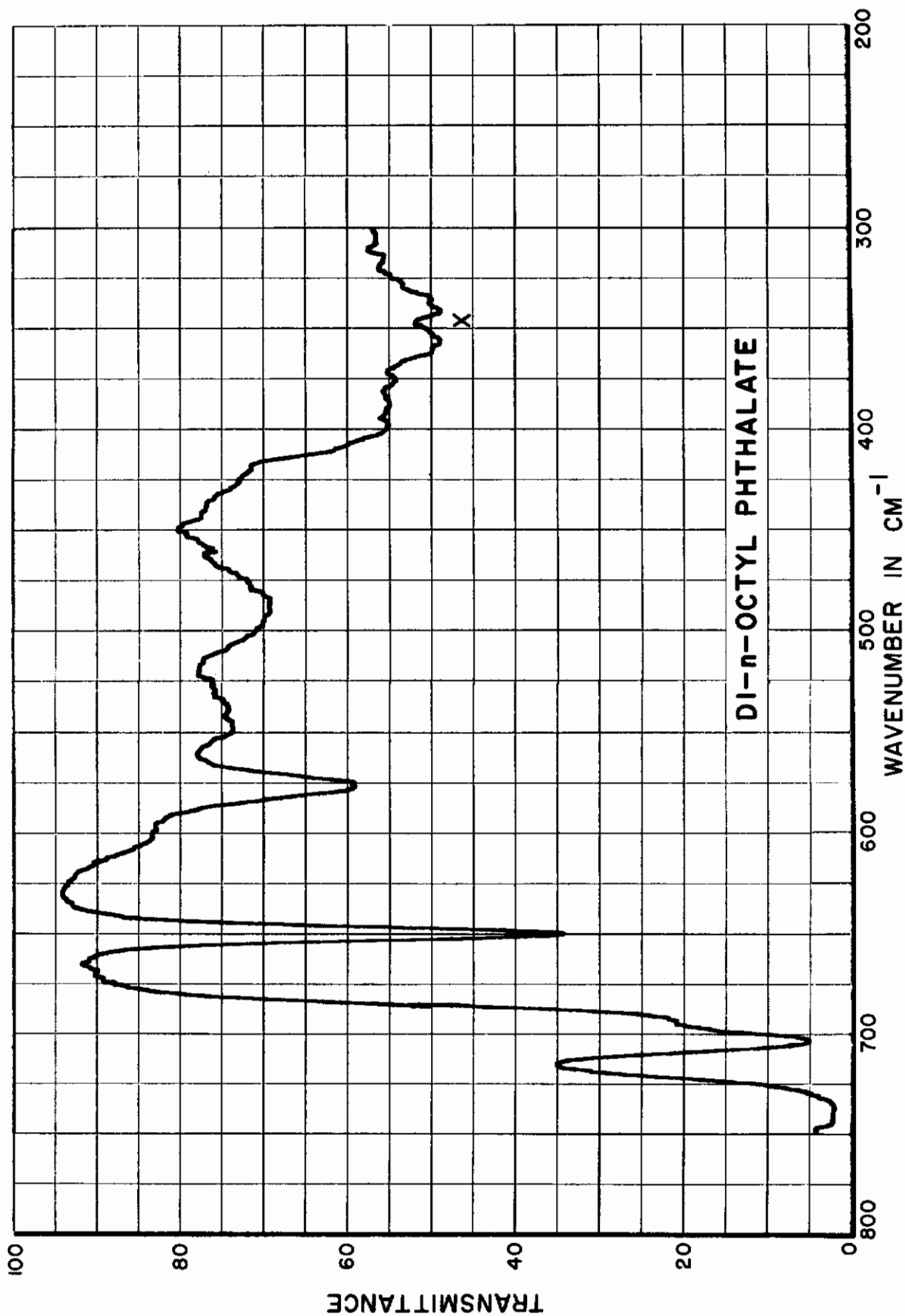


Figure 137. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Di-n-Octyl Phthalate  
Recorded using a 0.1 mm CsBr cell

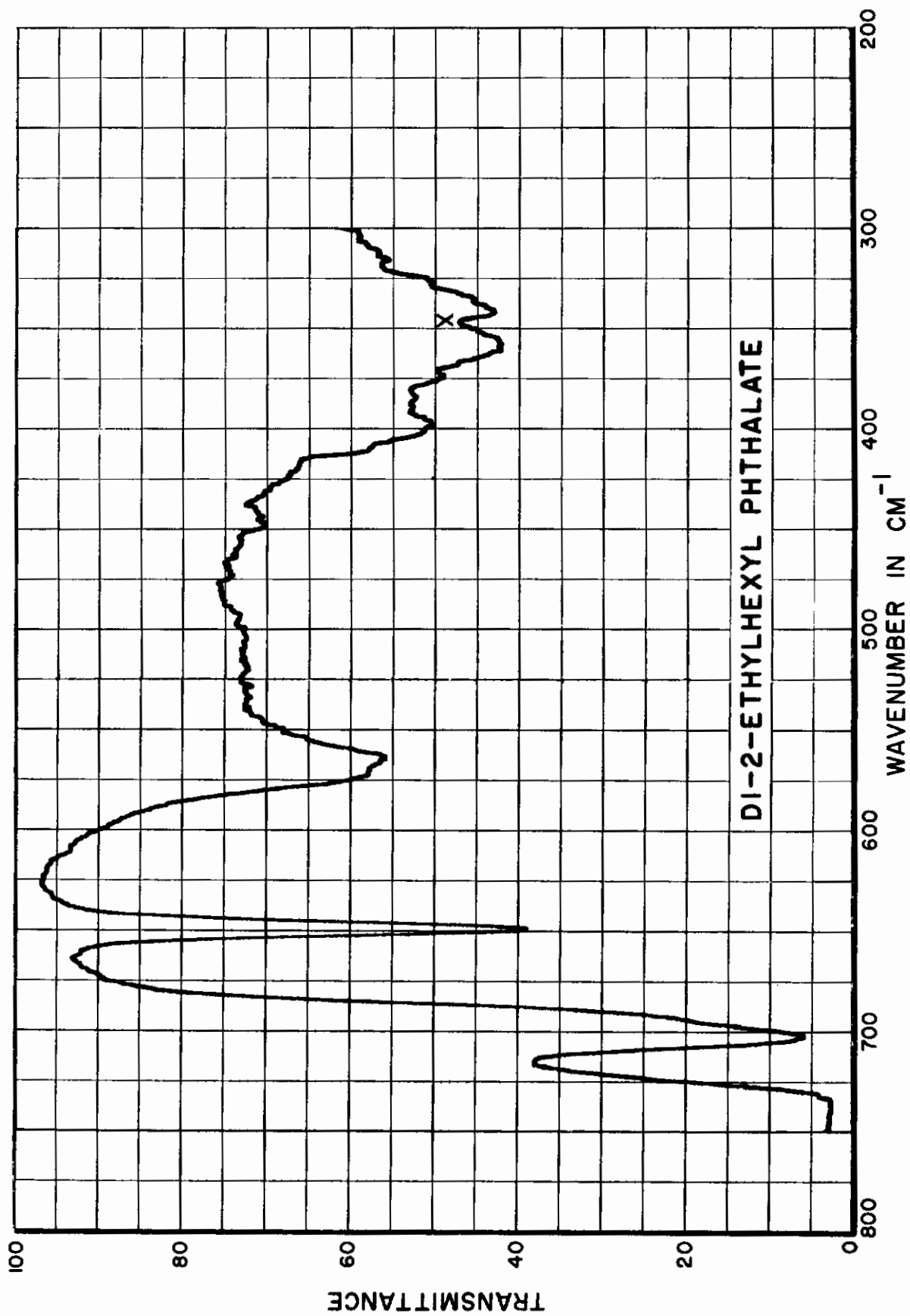


Figure 138. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Di-2-Ethylhexyl Phthalate  
Recorded using a 0.1 mm CsBr cell

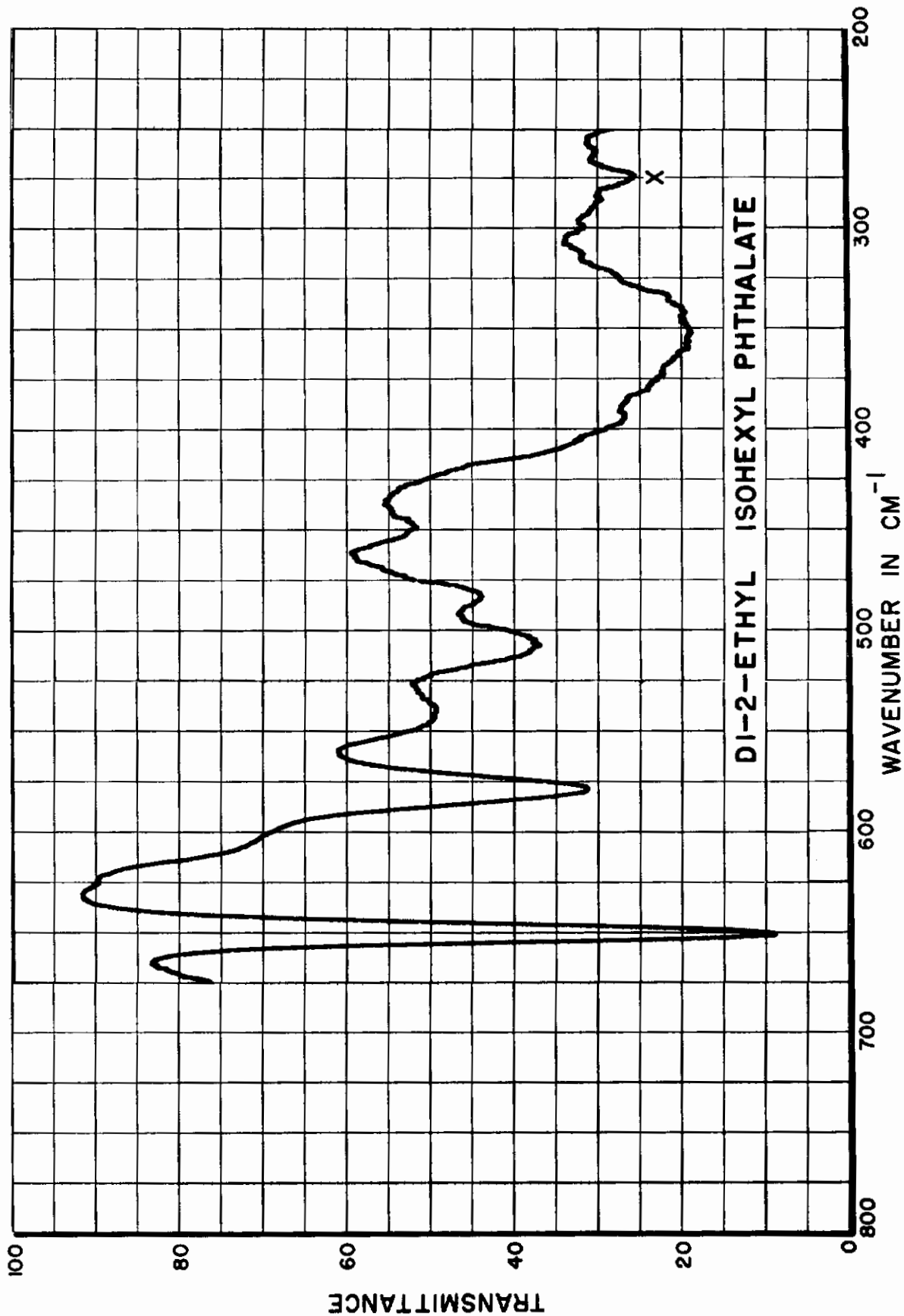


Figure 139. - Infrared Spectrum from 675 - 250 cm<sup>-1</sup> of Di-2-Ethyl Isohexyl Phthalate  
Recorded using a 0.21 mm CsBr cell



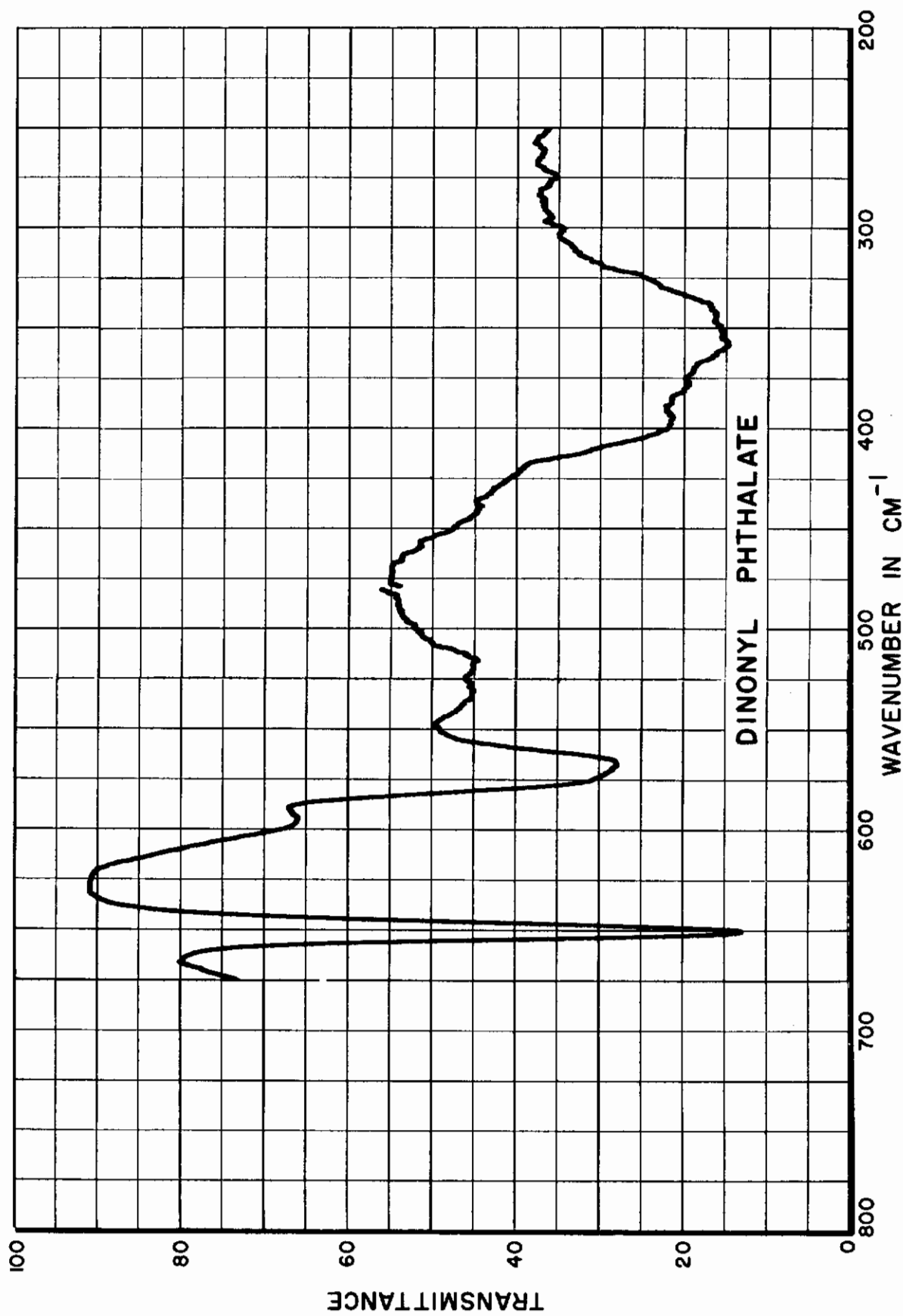


Figure 140. - Infrared Spectrum from 675 - 250 cm<sup>-1</sup> of Dinonyl Phthalate  
Recorded using a 0.2 mm CsBr cell

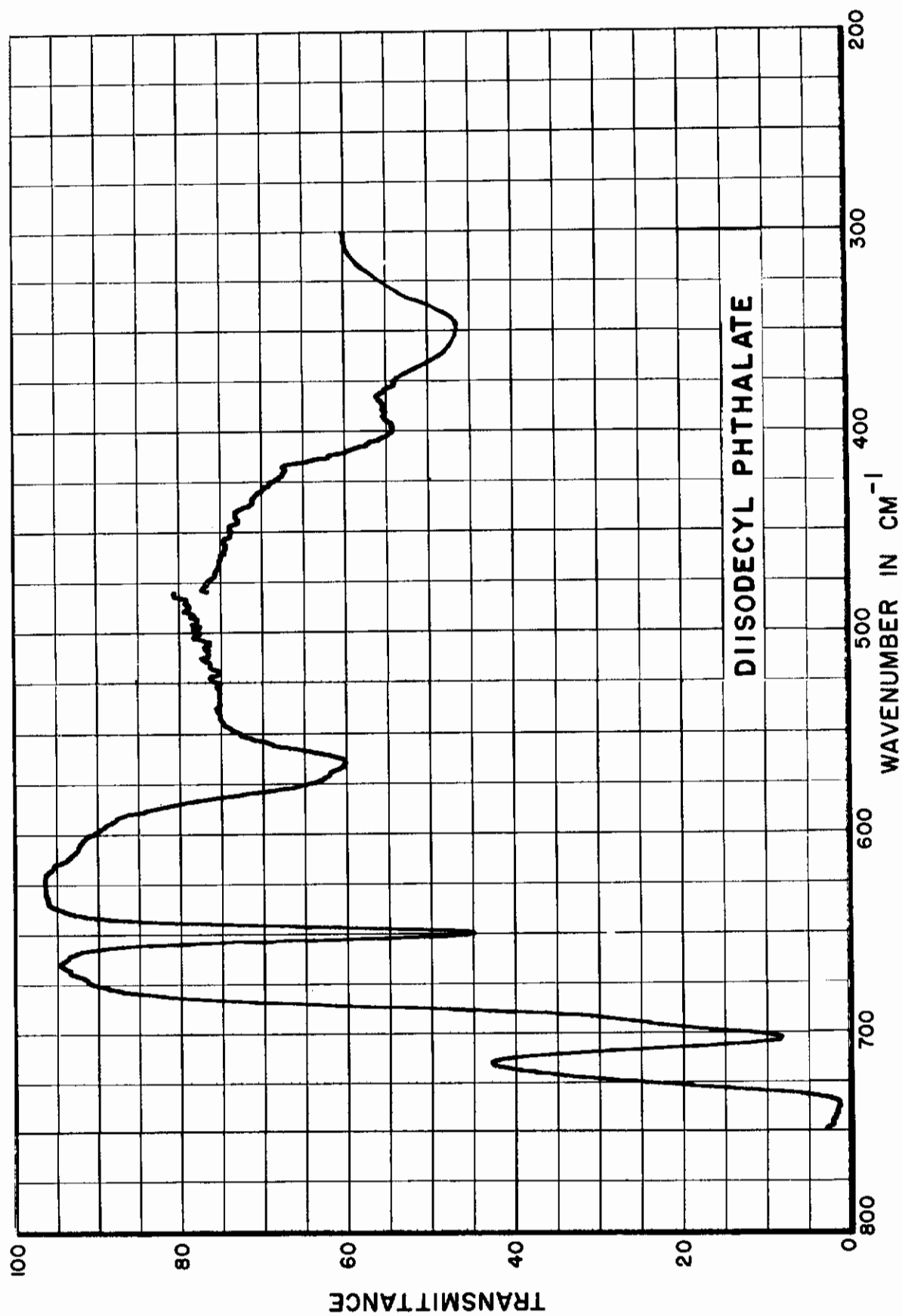


Figure 141. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Diisodecyl Phthalate (Santizer 214)  
Recorded using a 0.1 mm CsBr cell

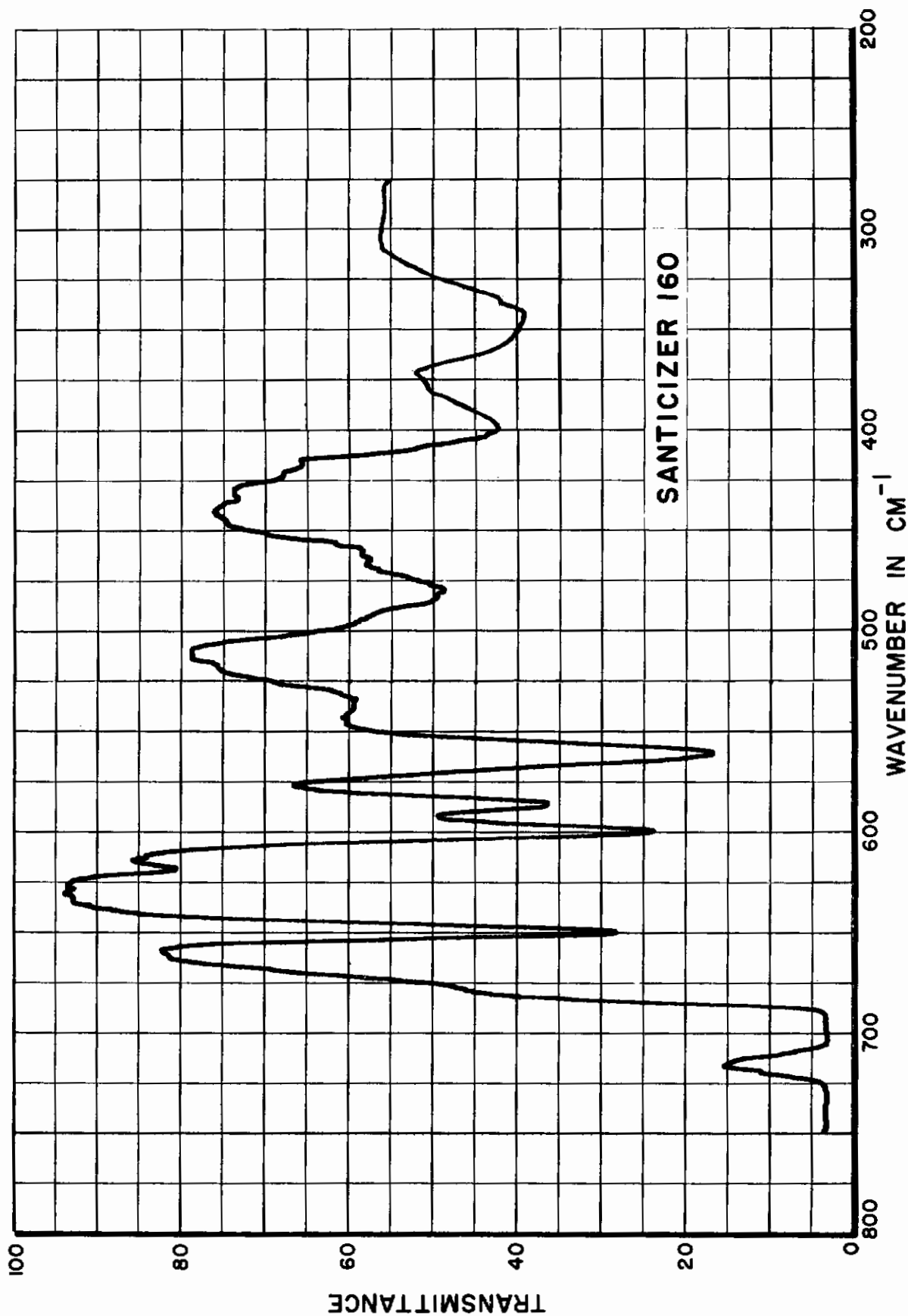


Figure 142. - Infrared Spectrum from 750 - 275 cm<sup>-1</sup> of Santicizer 160 (Butyl Benzyl Phthalate)  
Recorded using a 0.1 mm CsBr cell

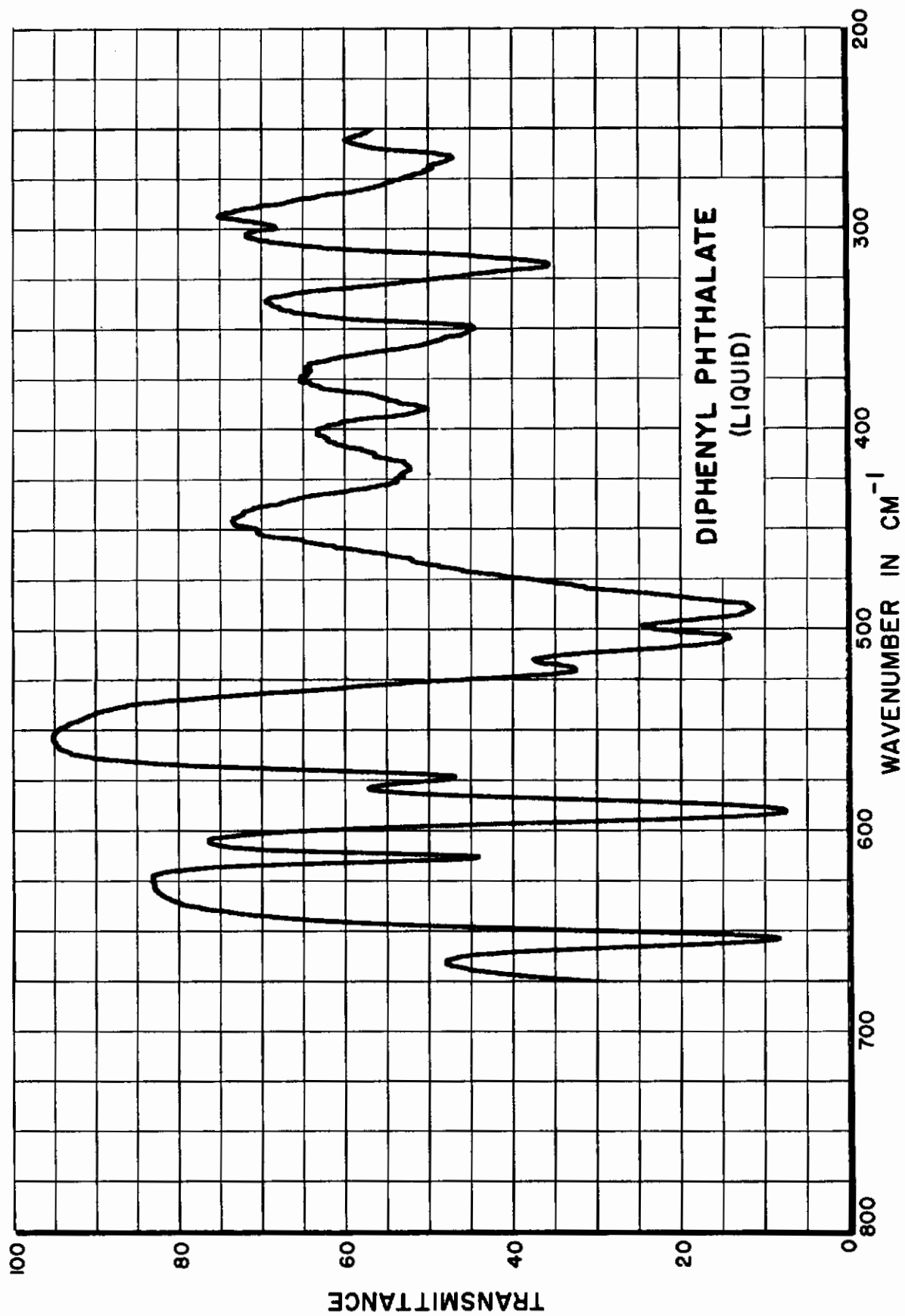


Figure 143. - Infrared Spectrum from 675 - 250 cm<sup>-1</sup> of Diphenyl Phthalate  
Recorded as a film

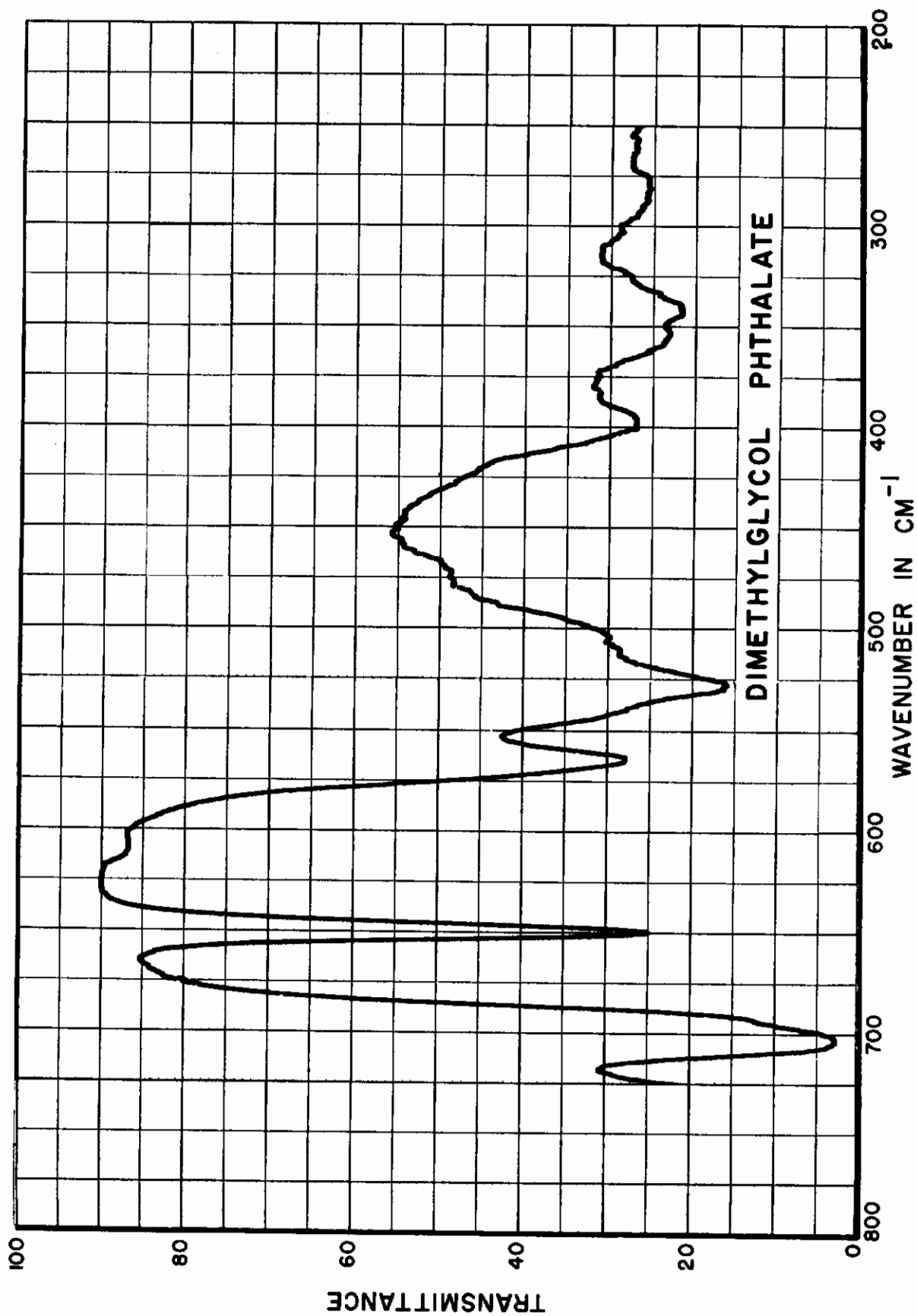


Figure 144. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Dimethylglycol Phthalate  
Recorded using a 0.1 mm CsBr cell

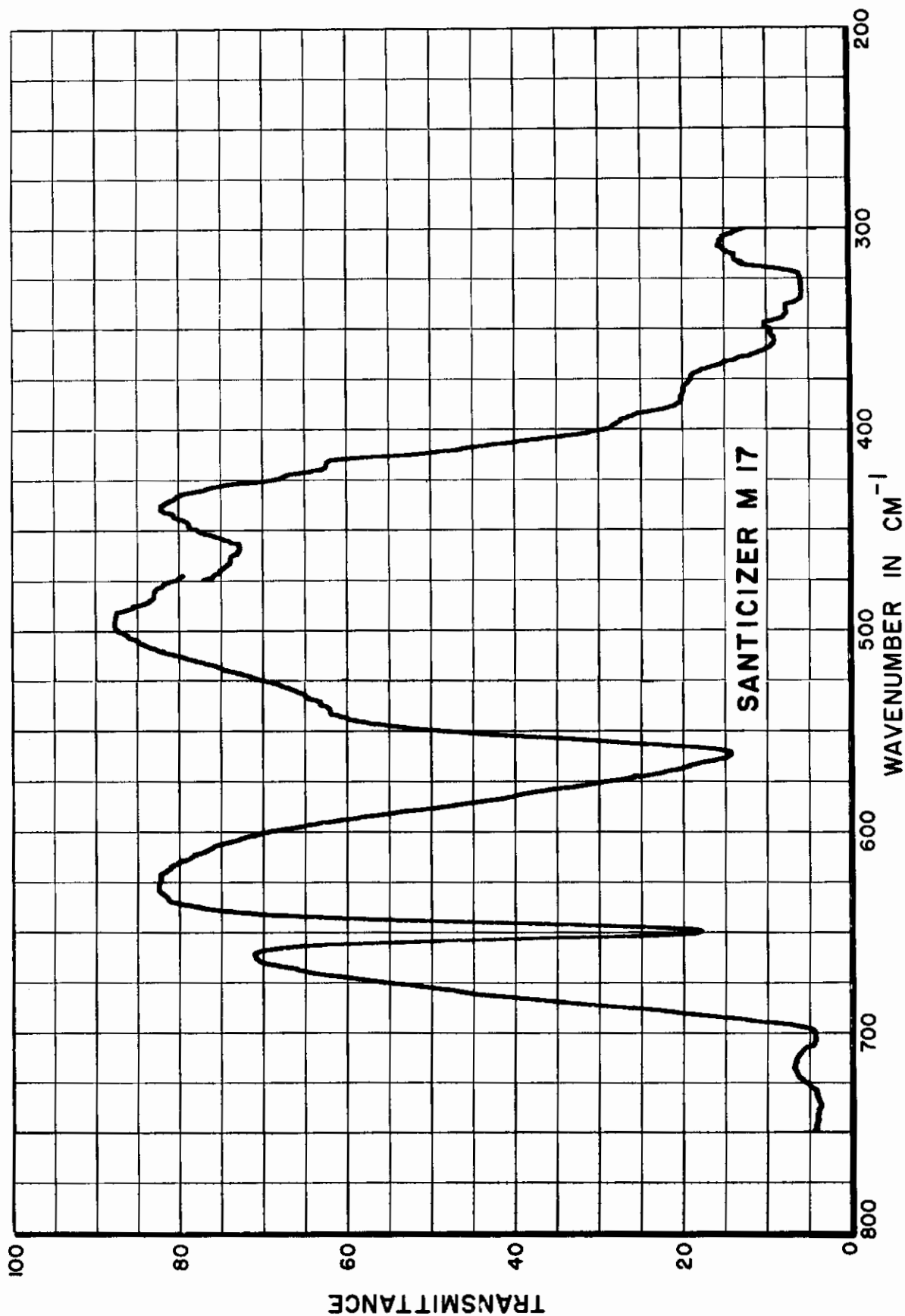


Figure 145. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Santicizer M 17 (Diethylphthalyl Ethylglycollate)  
Recorded using a 0.1 mm CsBr cell

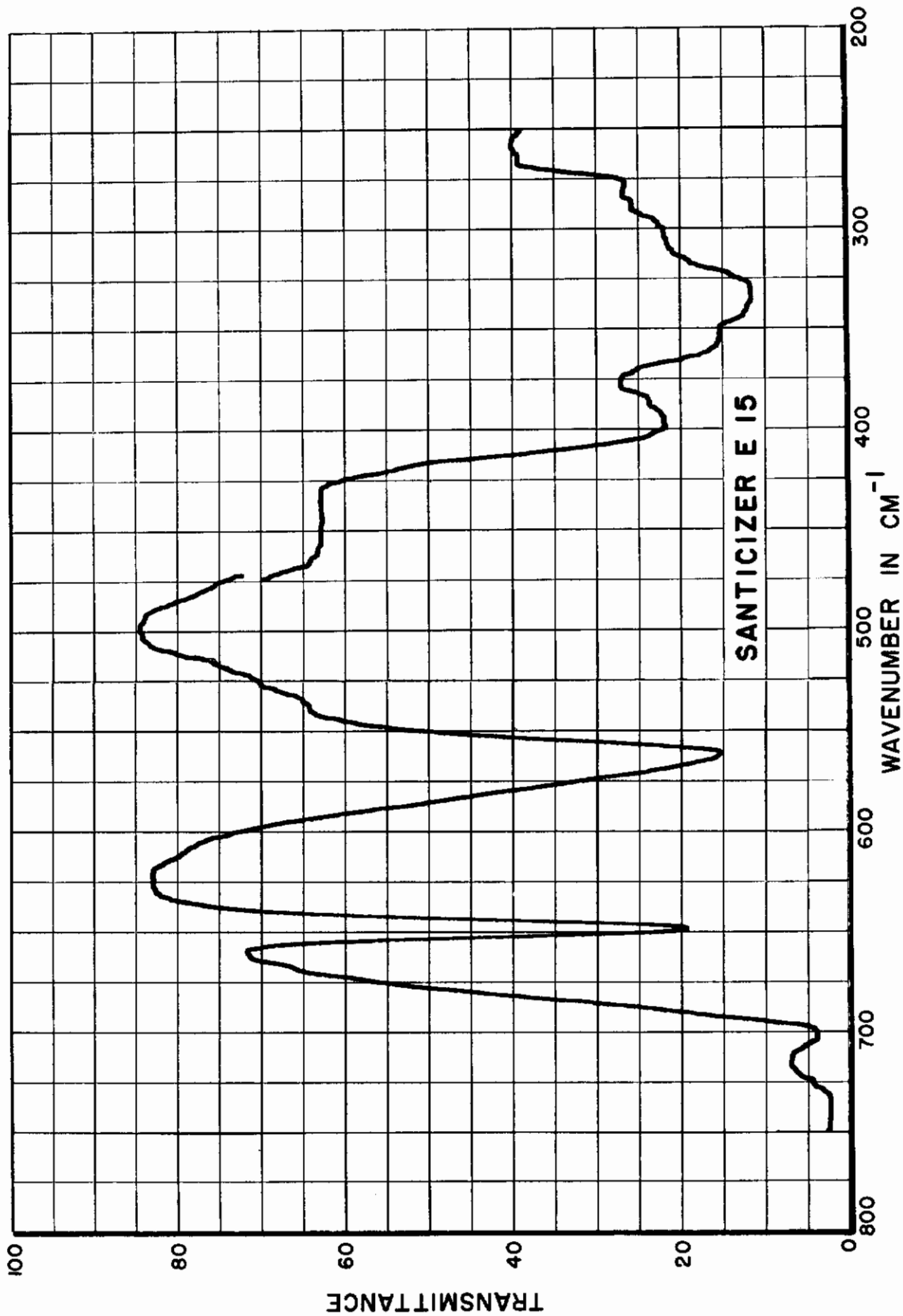


Figure 146. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Santicizer E 15 (Ethylphthalyl Ethylglycollate)

Recorded using a 0.1 mm CsBr cell

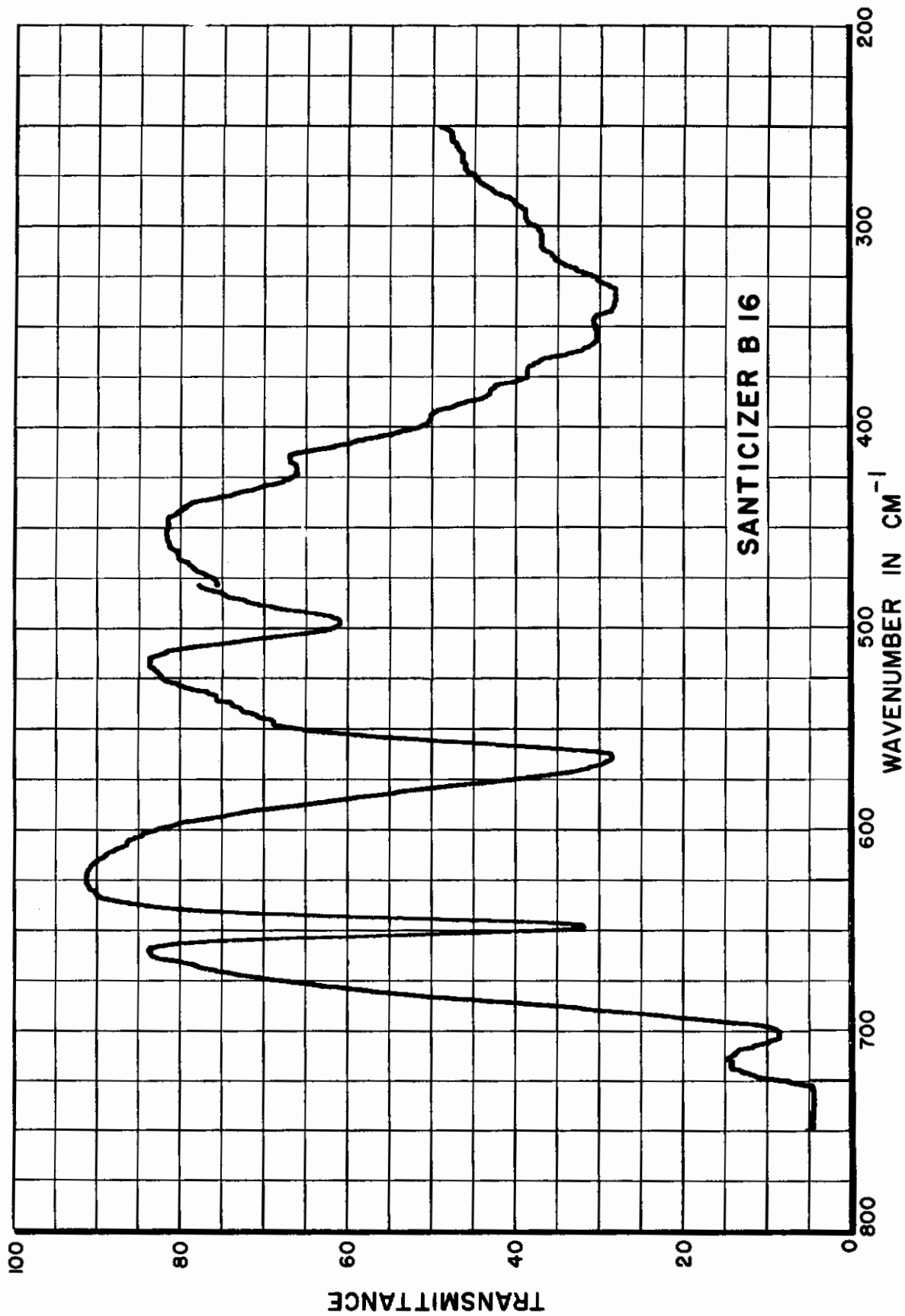
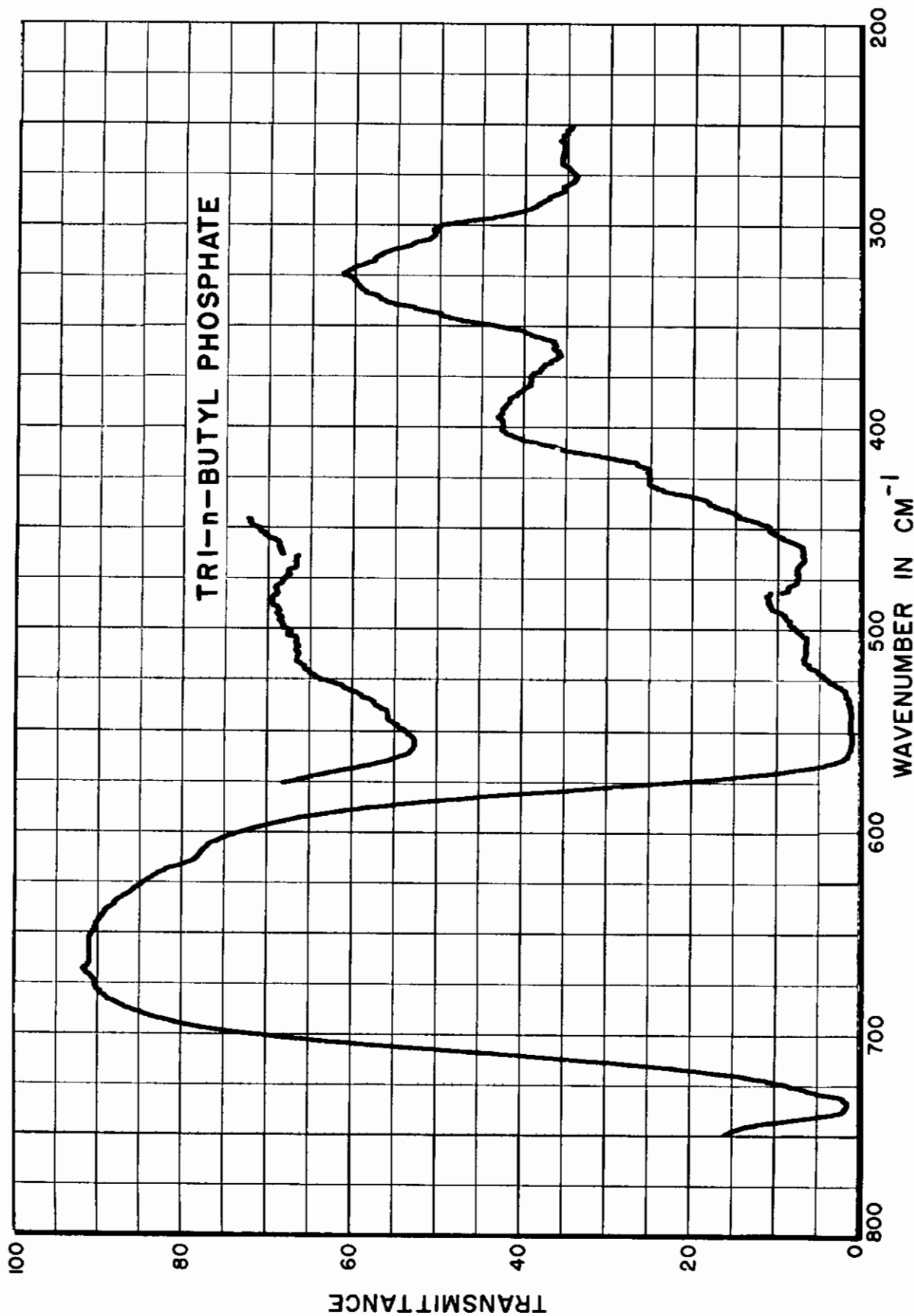


Figure 147. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Santicizer B 16 (Butylphthalyl Butylglycollate)  
Recorded using a 0.1 mm CsBr cell





TRI-n-BUTYL PHOSPHATE

Figure 148. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Tri-n-Butyl Phosphate  
Recorded using a 0.1 mm CsBr cell and as a capillary film

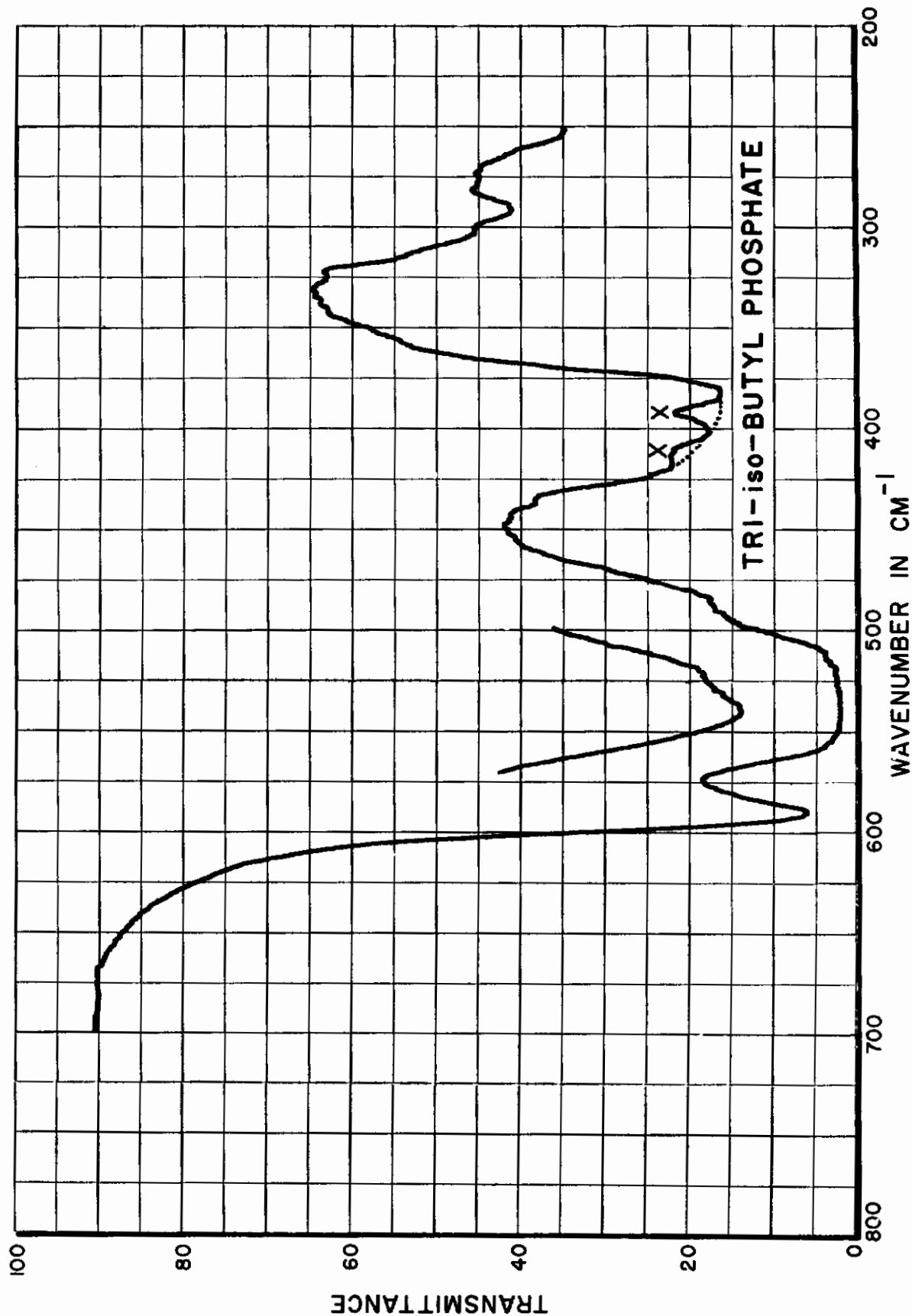


Figure 149. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Triisobutyl Phosphate  
Recorded using a 0.1 mm CsBr cell and as a capillary film

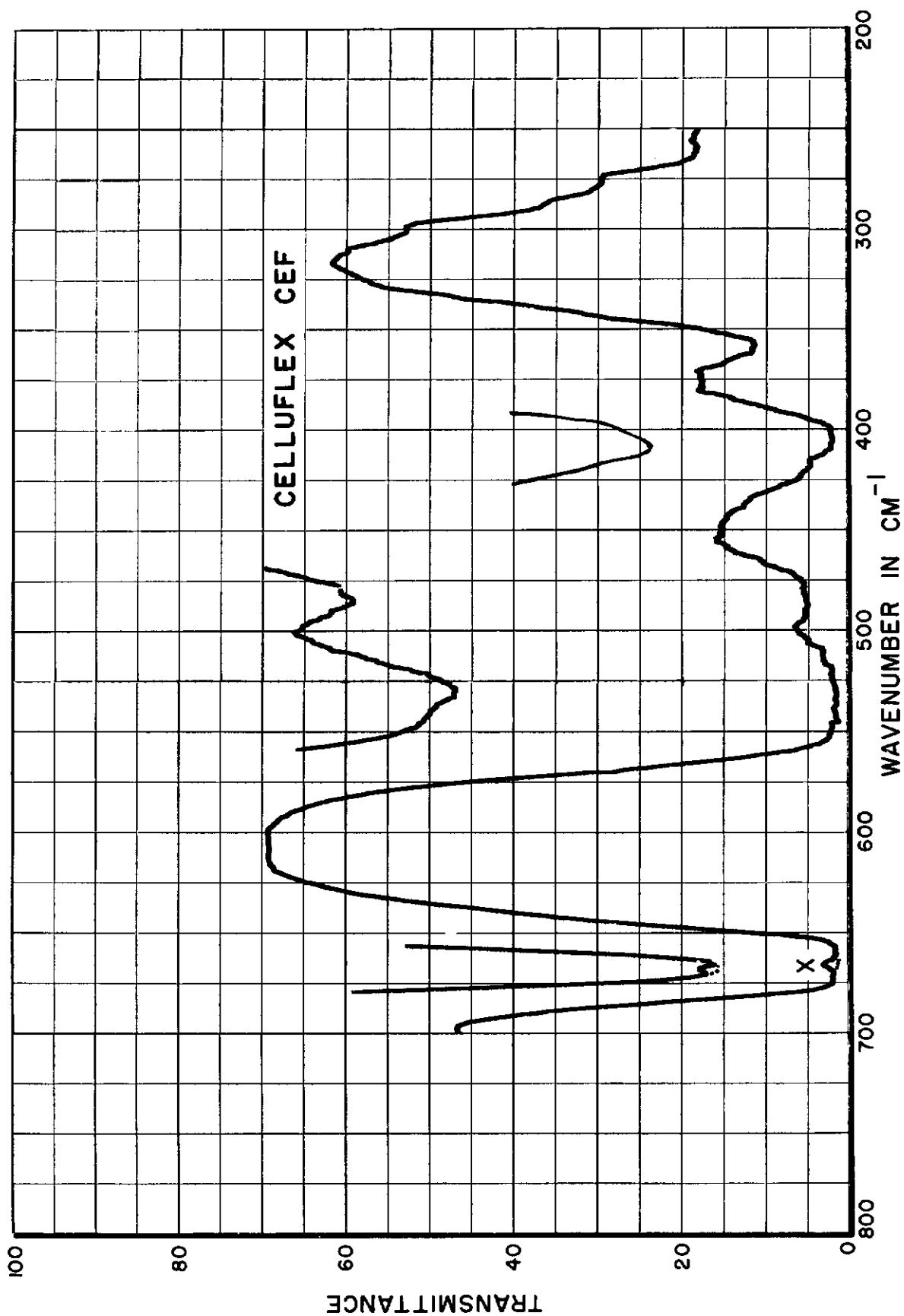


Figure 150. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Celluflex CEF (Tris( $\beta$ -Chloroethyl)Phosphate) Recorded using a 0.1 mm CsBr cell and as a capillary film

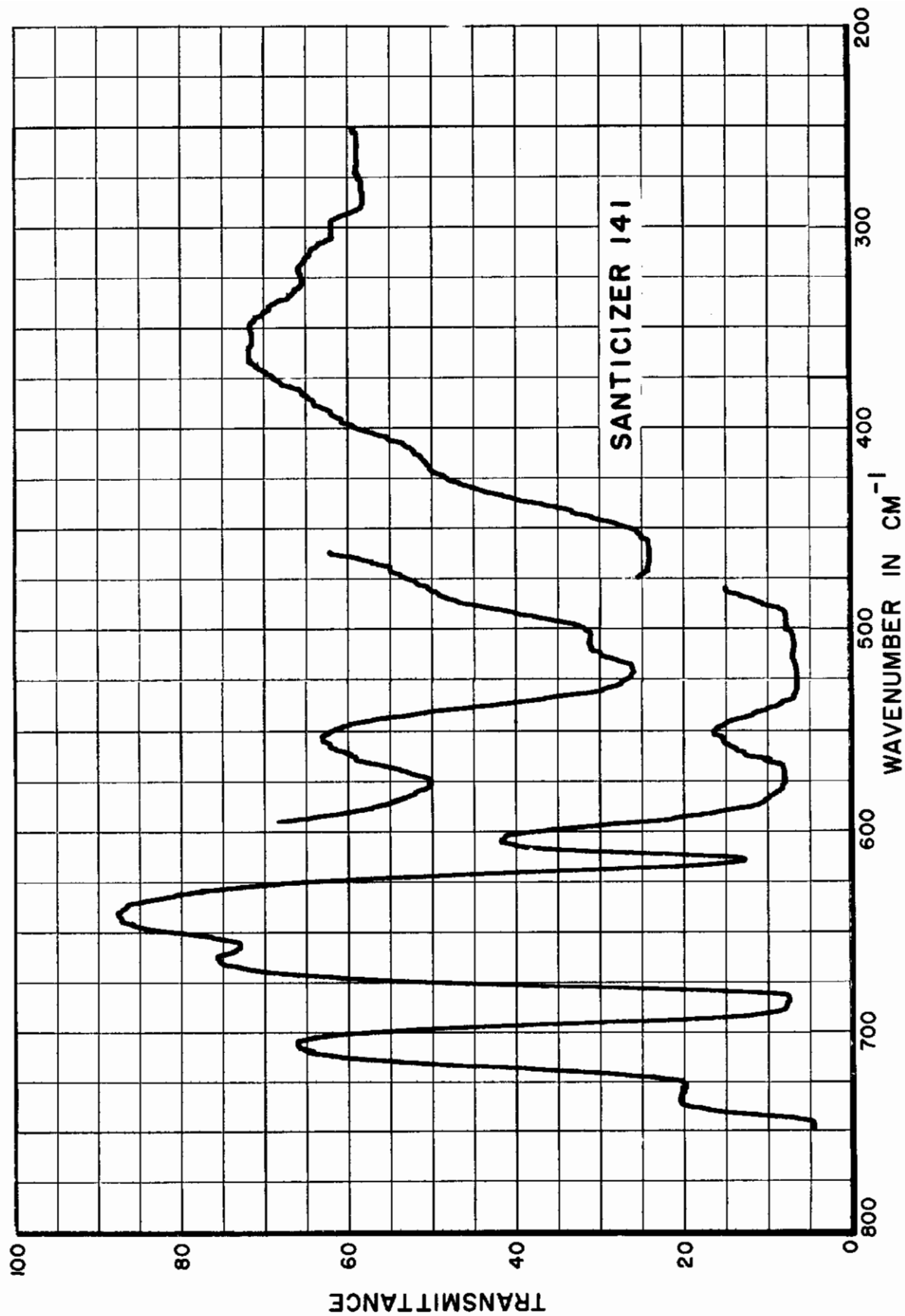


Figure 151. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Santicizer 141 (2-Ethylhexyl Diphenyl Phosphate)  
Recorded using a 0.1 mm CsBr cell and as a capillary film

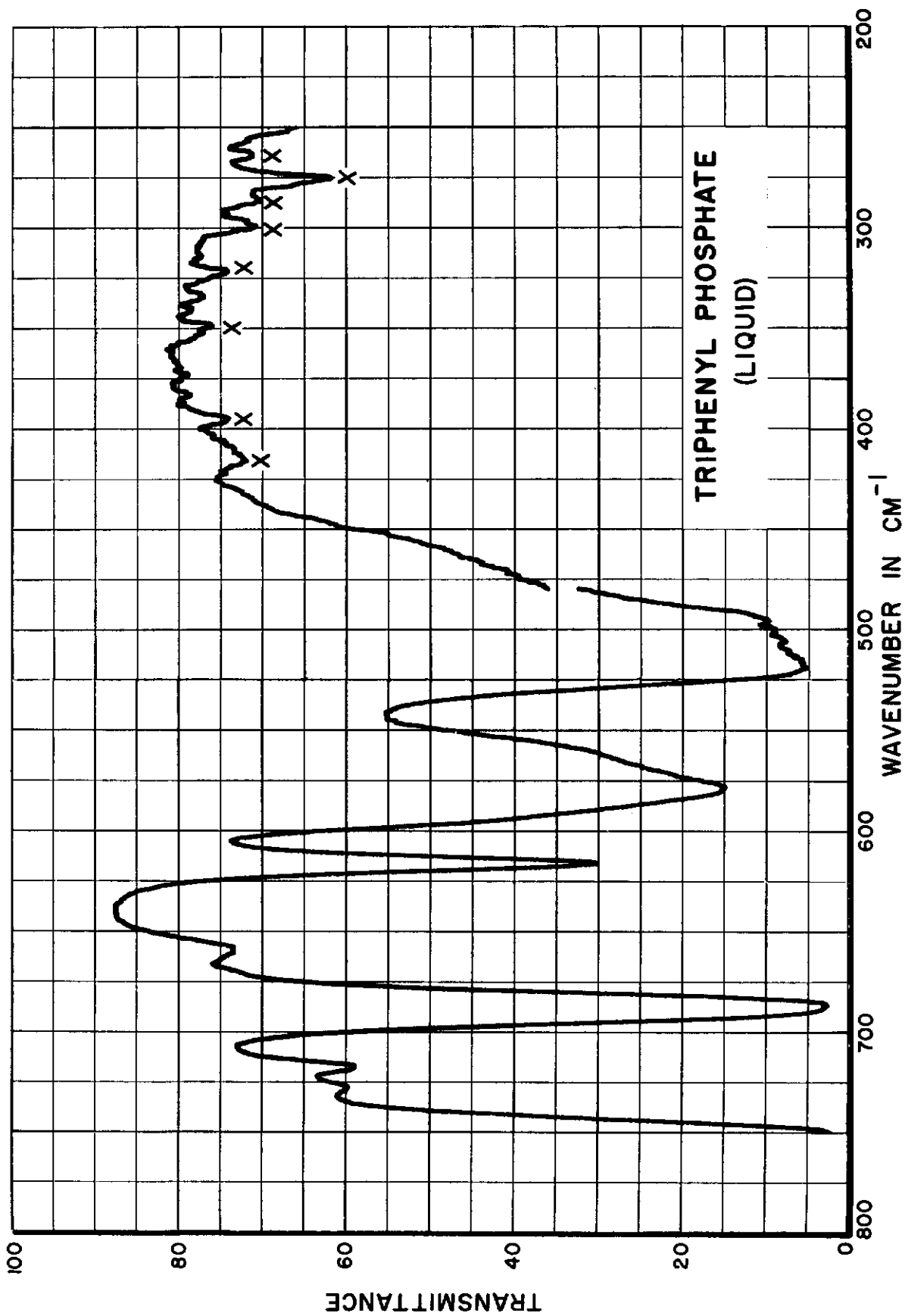


Figure 152. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Triphenyl Phosphate  
Recorded as a film

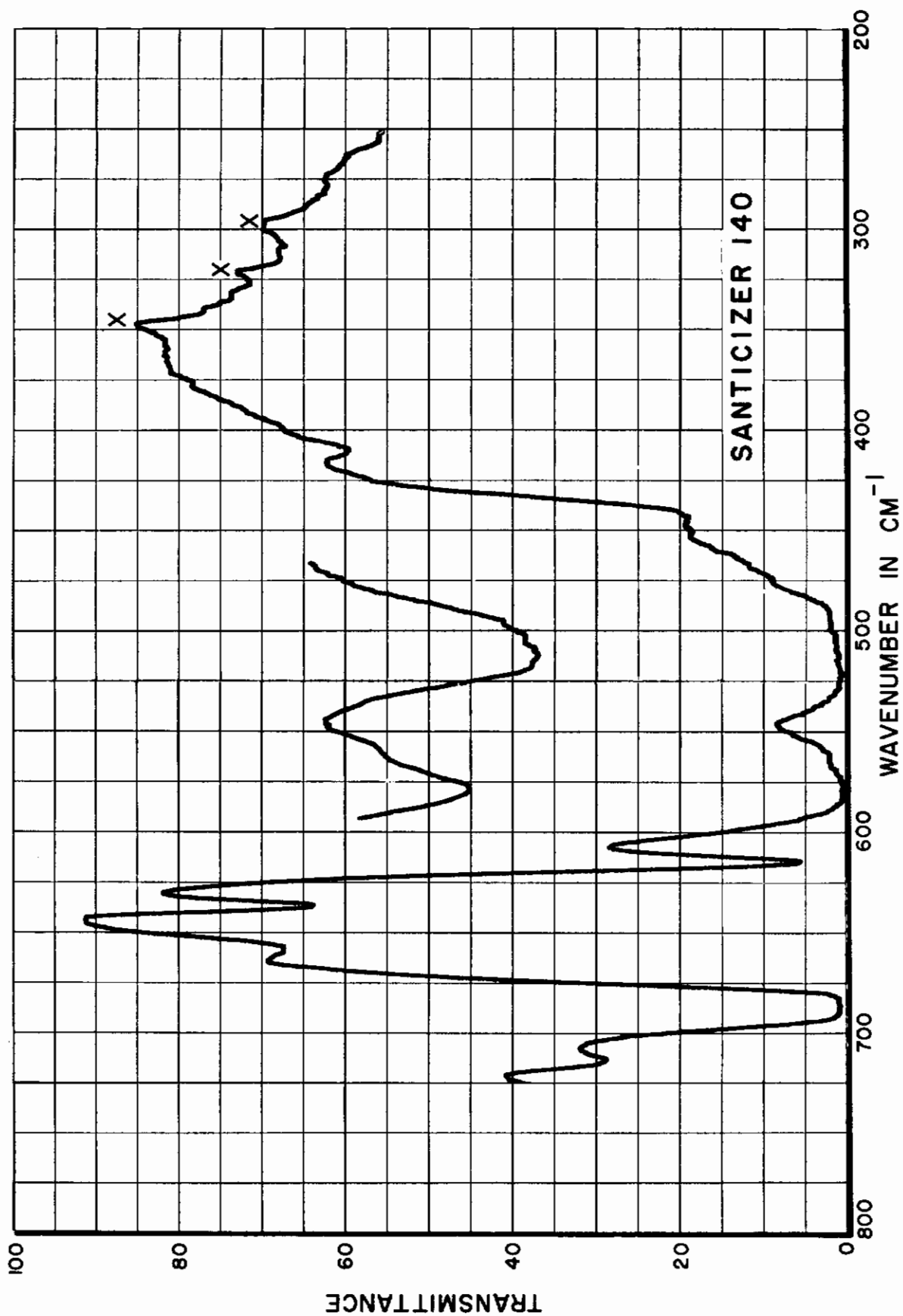


Figure 153. - Infrared Spectrum from 725 - 250 cm<sup>-1</sup> of Santicizer 140 (Cresyl Diphenyl Phosphate) Recorded using a 0.1 mm CsBr cell and as a capillary film

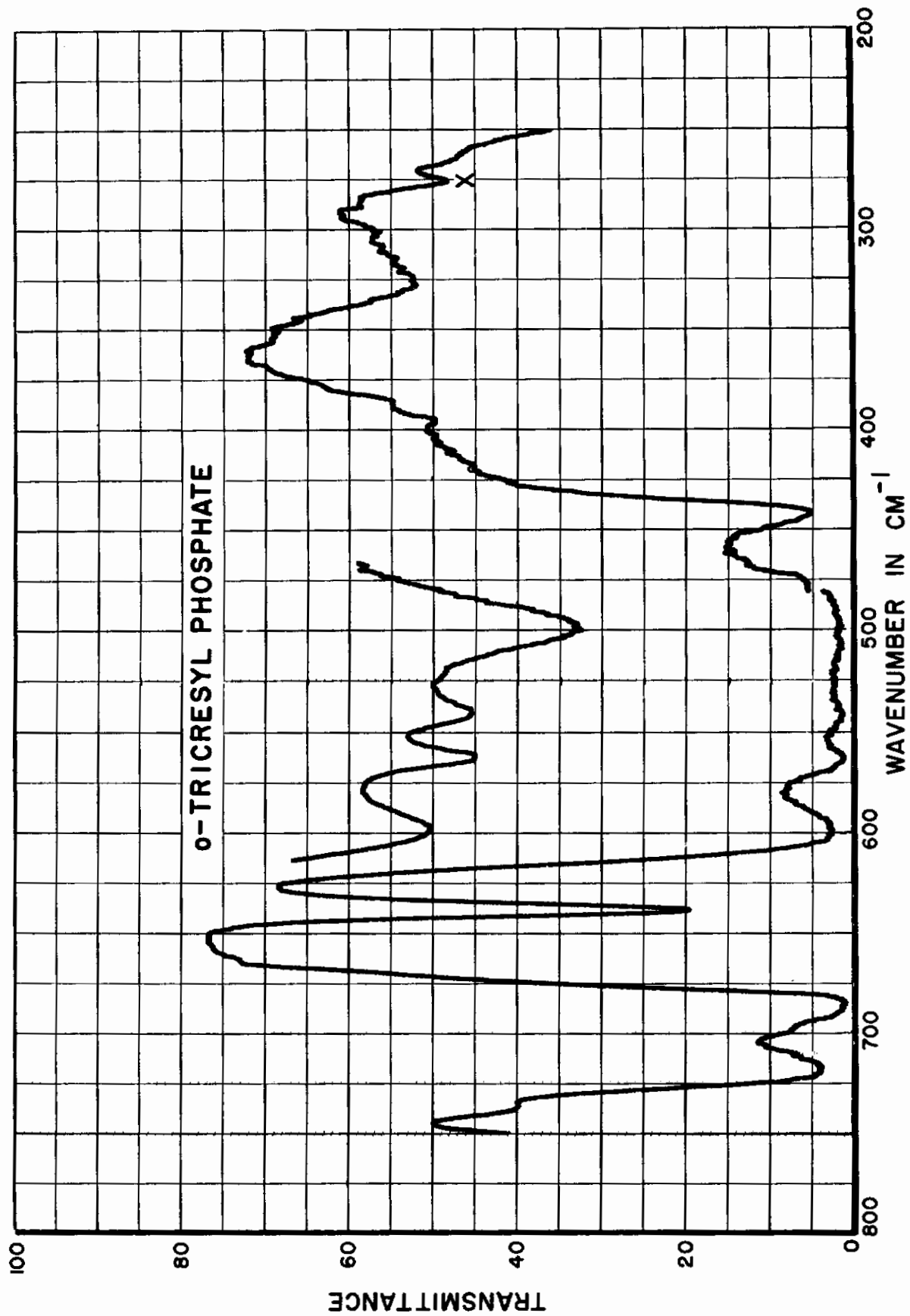


Figure 154. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of o-Tricresyl Phosphate  
Recorded using a 0.1 mm CsBr cell and as a capillary film

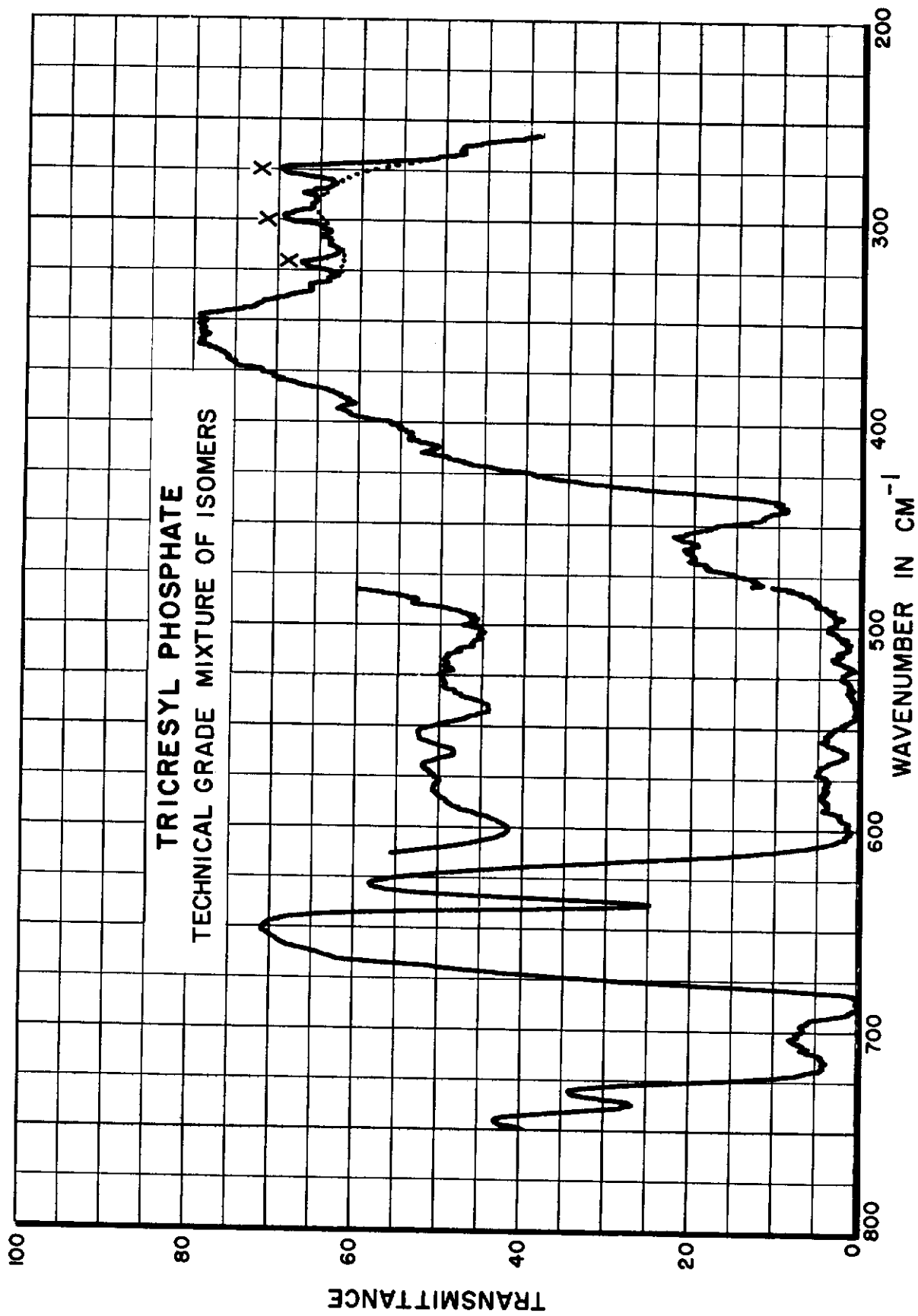


Figure 155. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Tricresyl Phosphate (Technical Grade, Mixture of Isomers)

Recorded using a 0.1 mm CsBr cell and as a capillary film



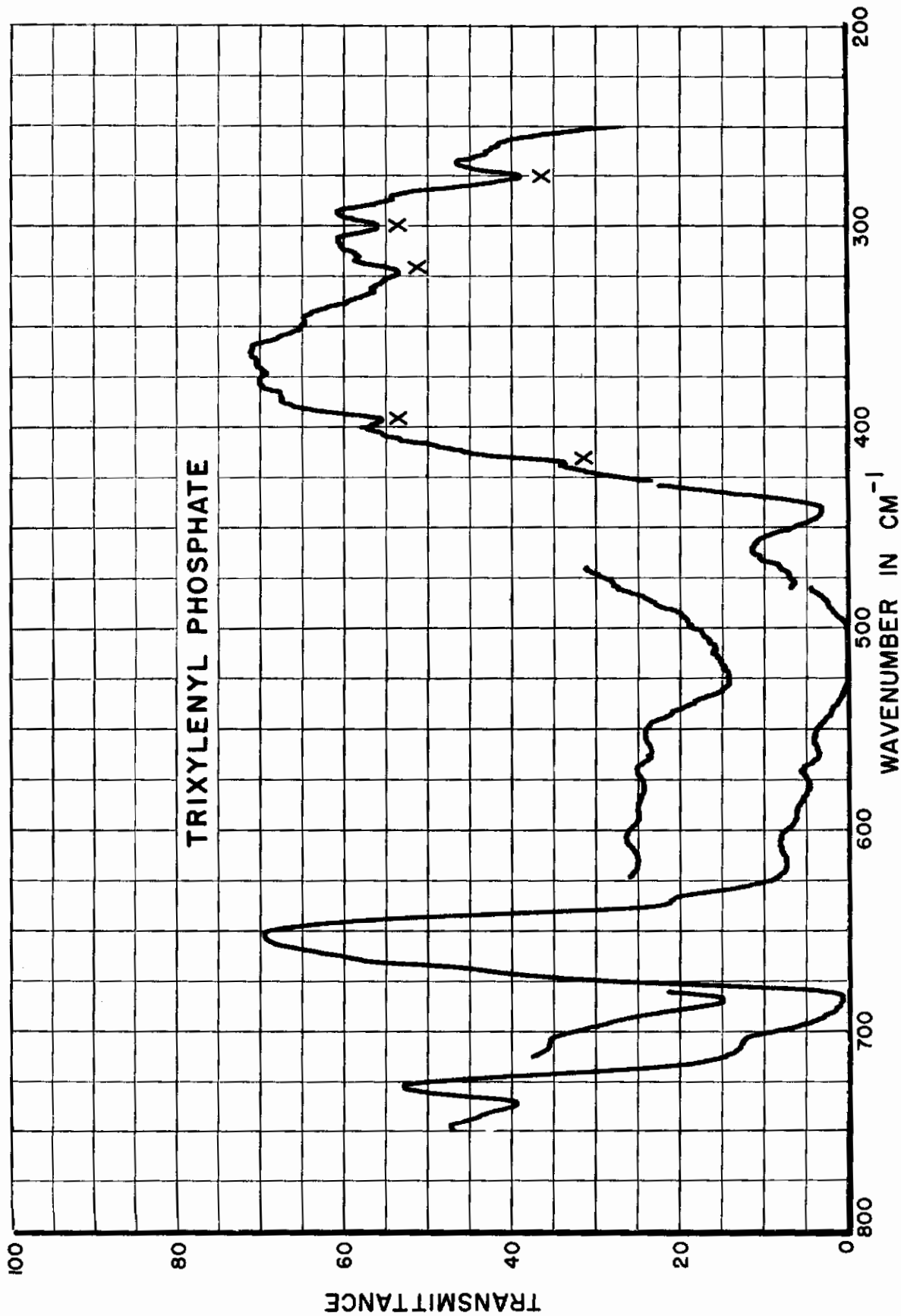


Figure 156. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Trixylenyl Phosphate  
Recorded using a 0.1 mm CsBr cell and as a capillary film

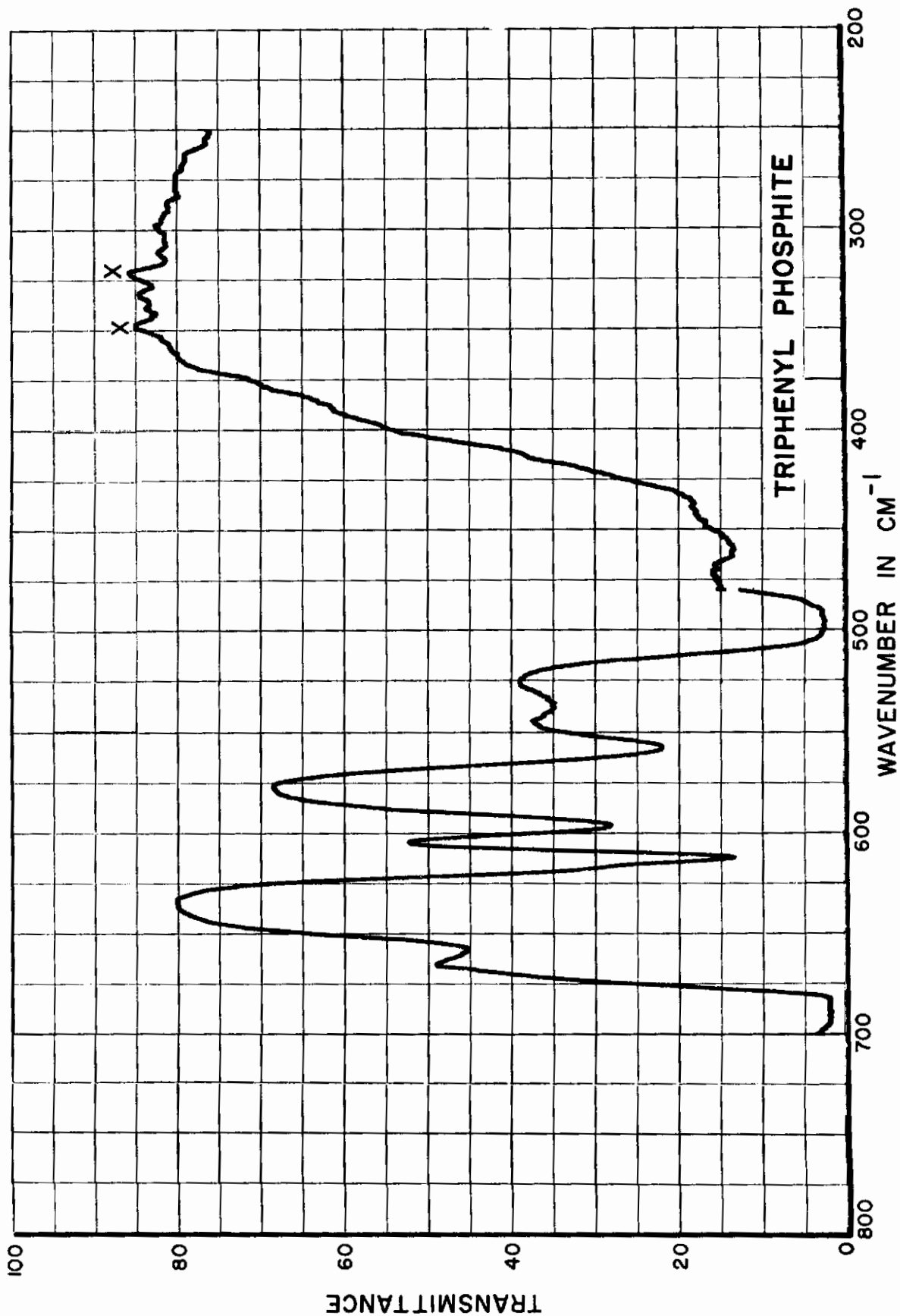


Figure 157. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Triphenyl Phosphite  
Recorded using a 0.1 mm CsBr cell

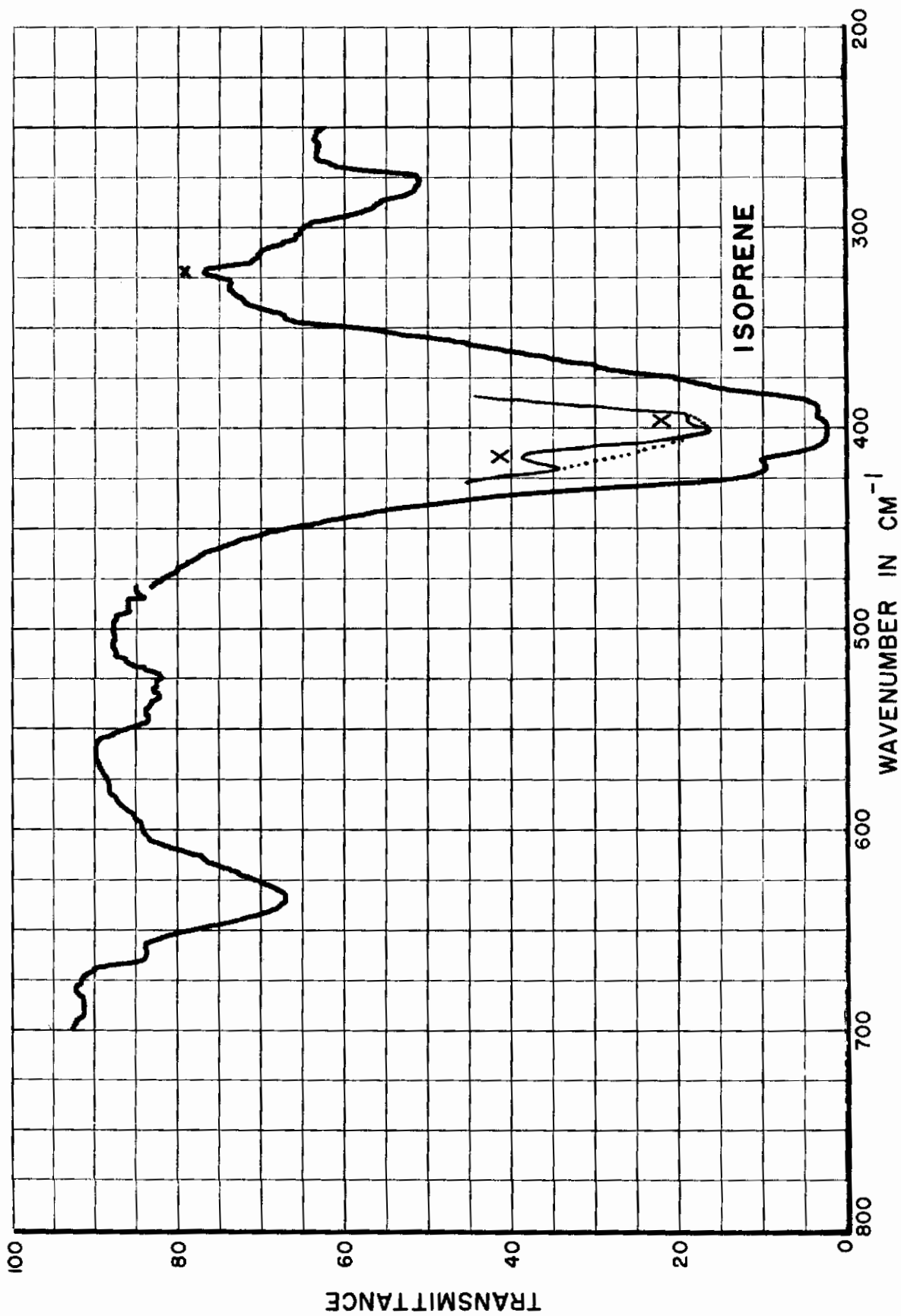


Figure 158. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Isoprene  
Recorded using 0.1 and 0.21 mm CsBr cells

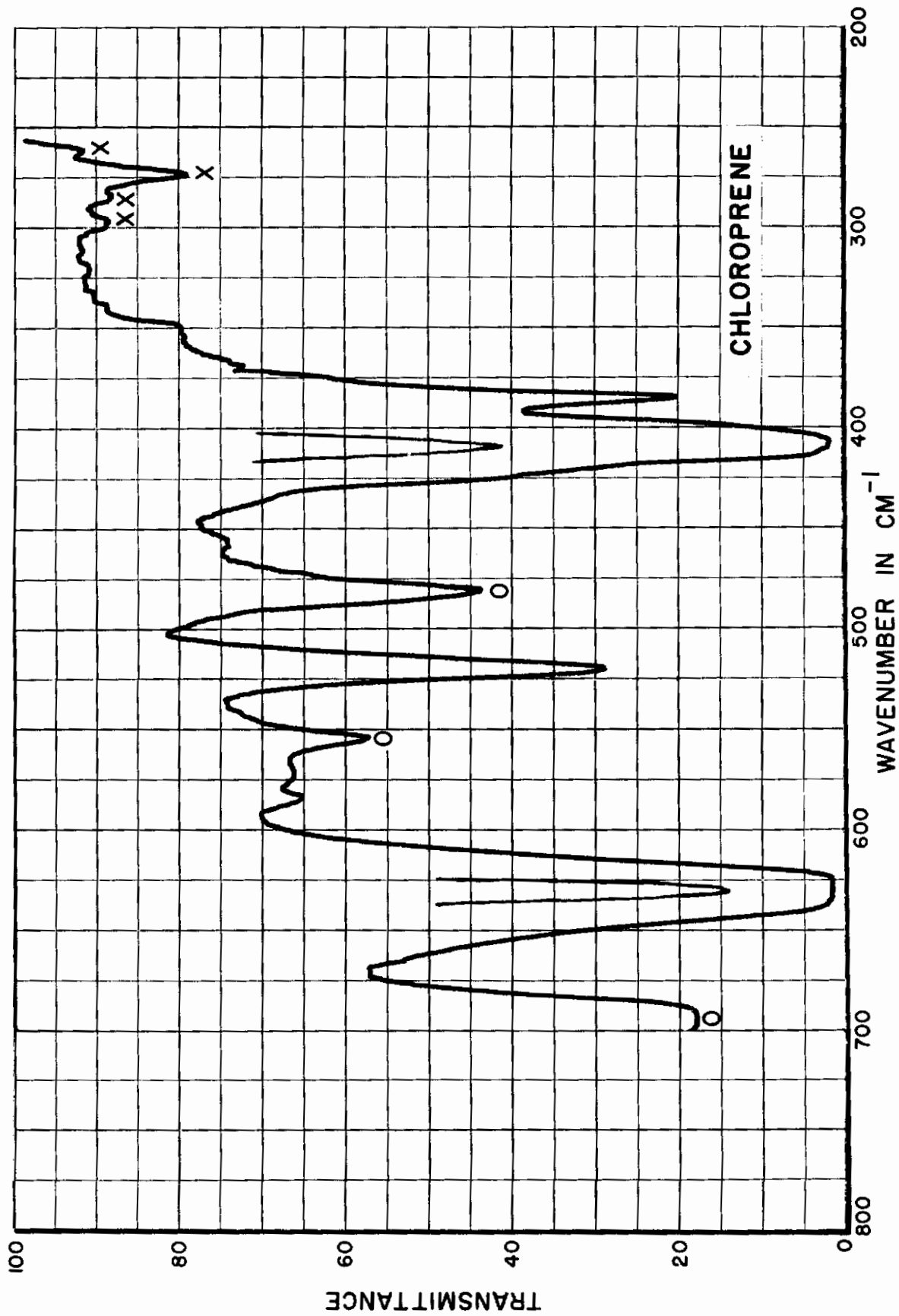


Figure 159. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Chloroprene (2-Chlorobutadiene)  
Recorded using 0.1 and 0.21 mm CsBr cells  
The bands designated with an "o" are due to toluene

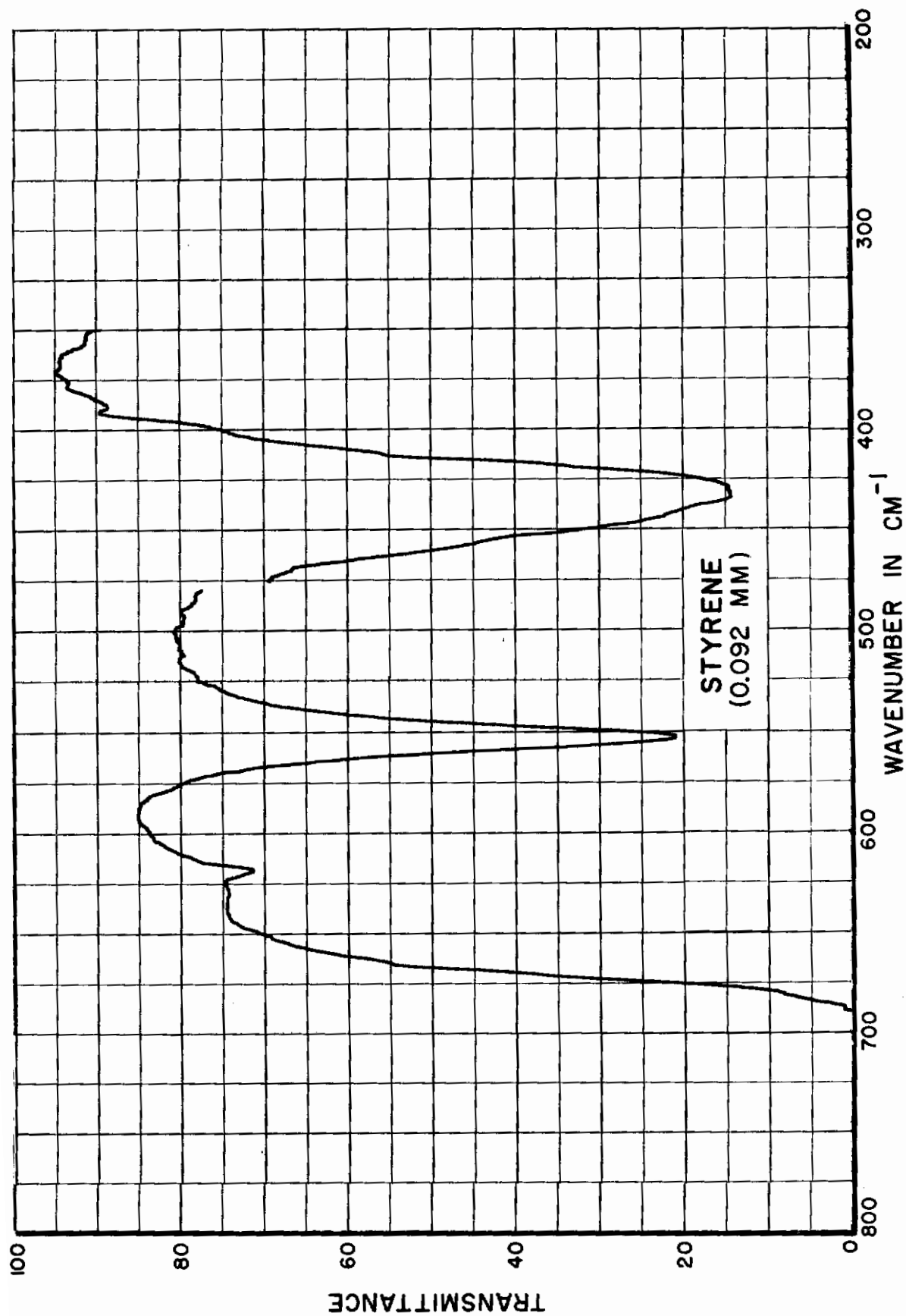


Figure 160. - Infrared Spectrum from 700 - 350 cm<sup>-1</sup> of Styrene  
Recorded using a 0.092 mm CsBr cell

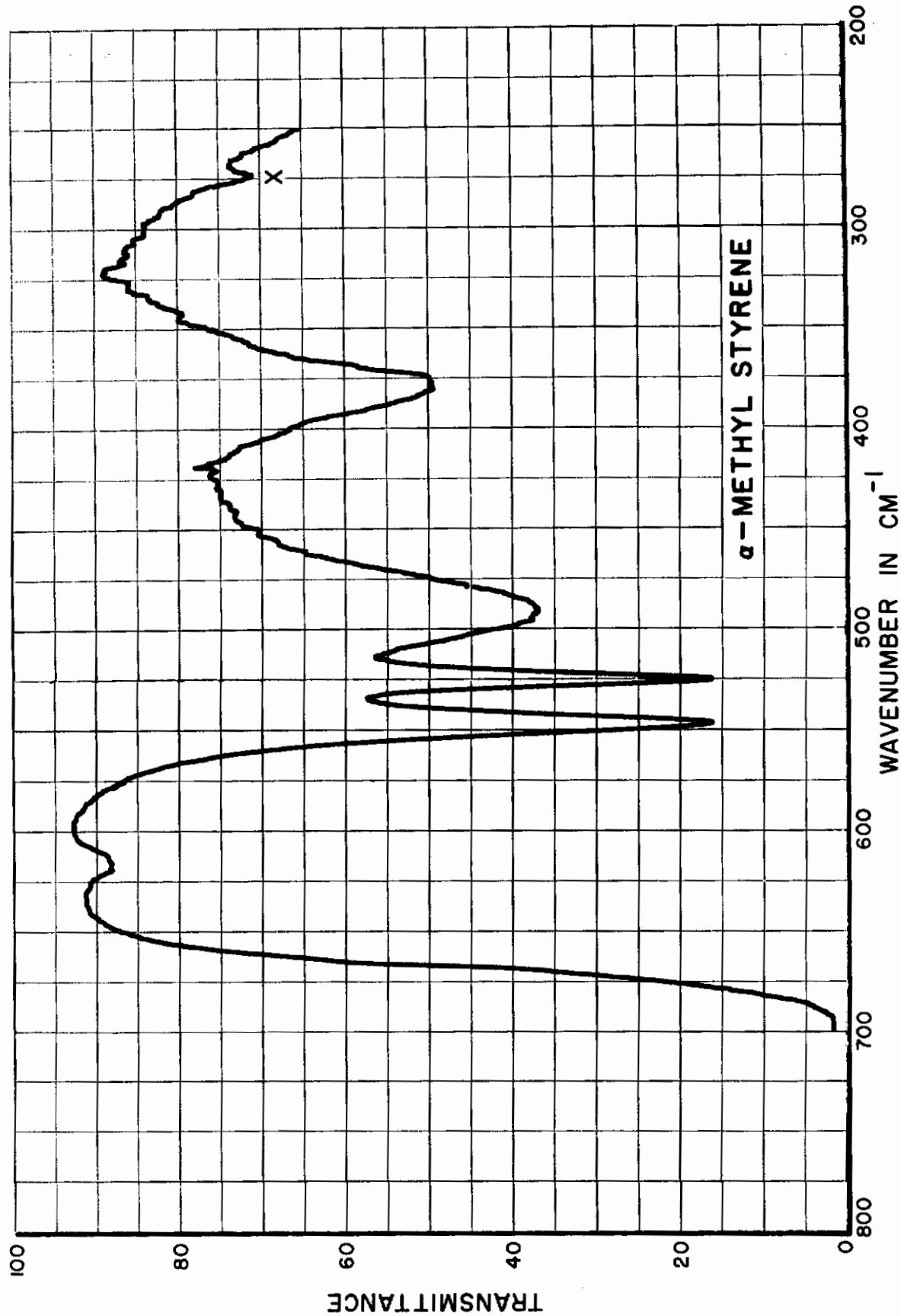


Figure 161. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of  $\alpha$ -Methyl Styrene  
Recorded using a 0.1 mm CsBr cell

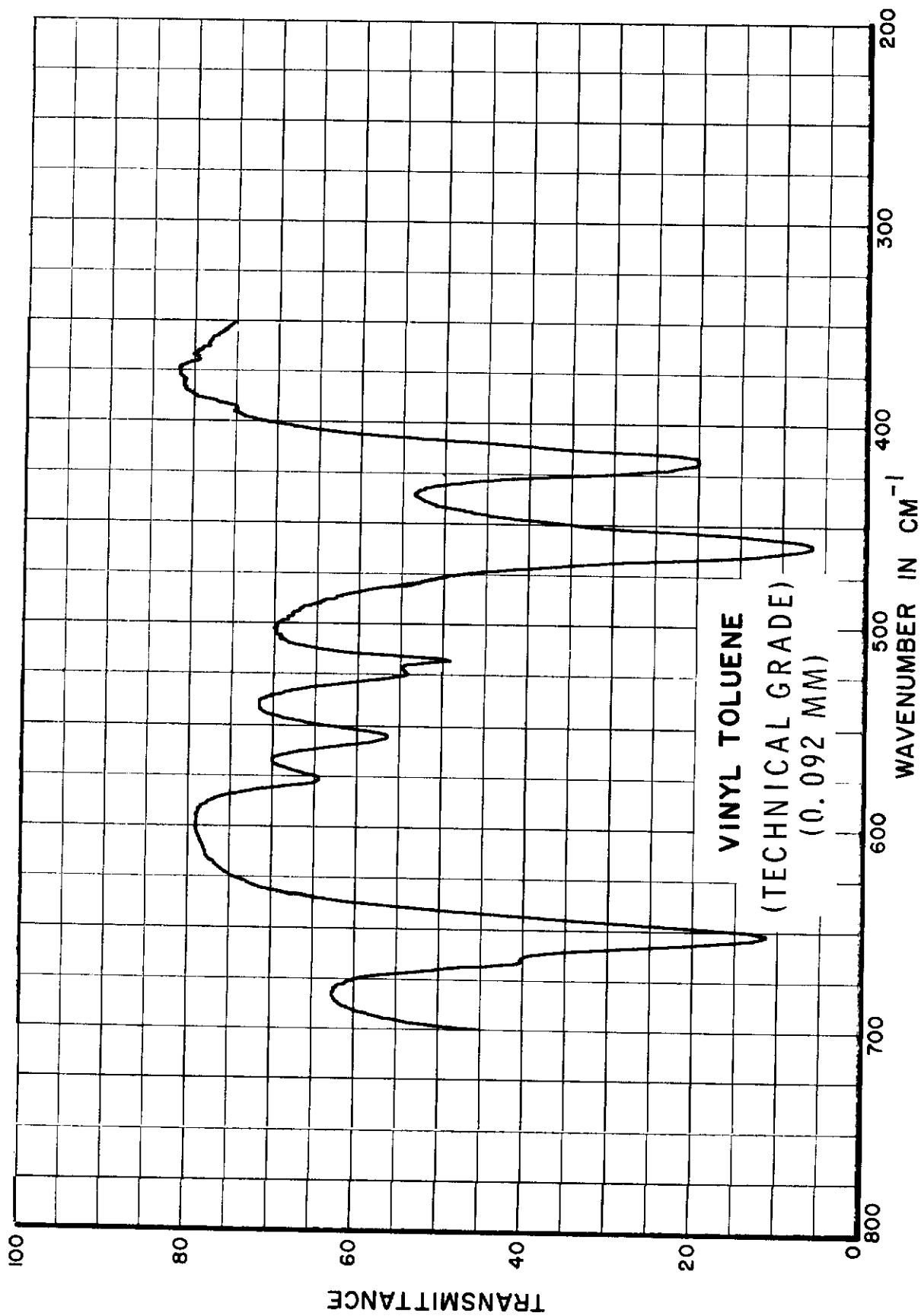


Figure 162. - Infrared Spectrum from 700 - 350  $\text{cm}^{-1}$  of Vinyl Toluene (Technical Grade)  
Recorded using a 0.092 mm CsBr cell

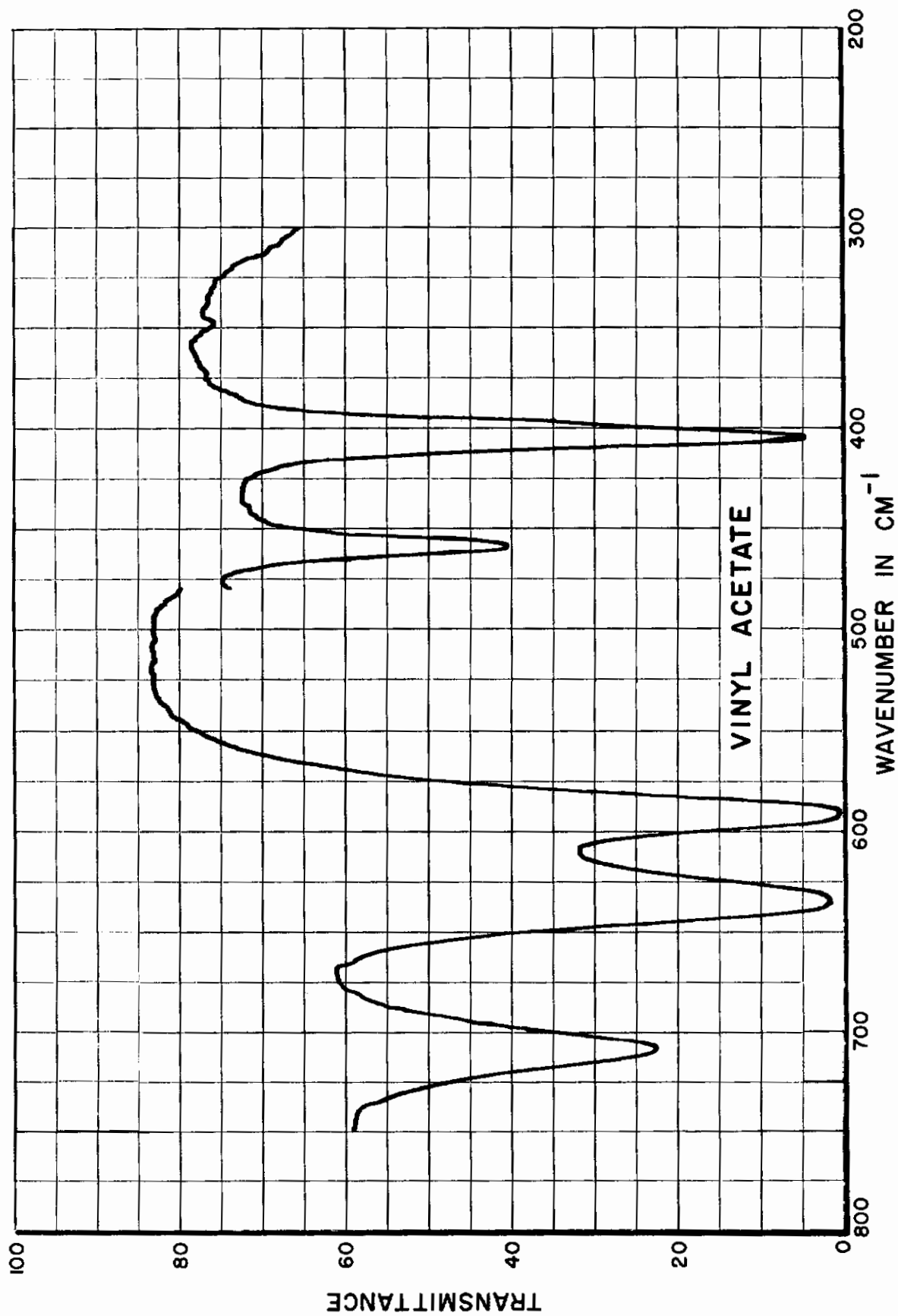


Figure 163. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Vinyl Acetate  
Recorded using a 0.1 mm CsBr cell



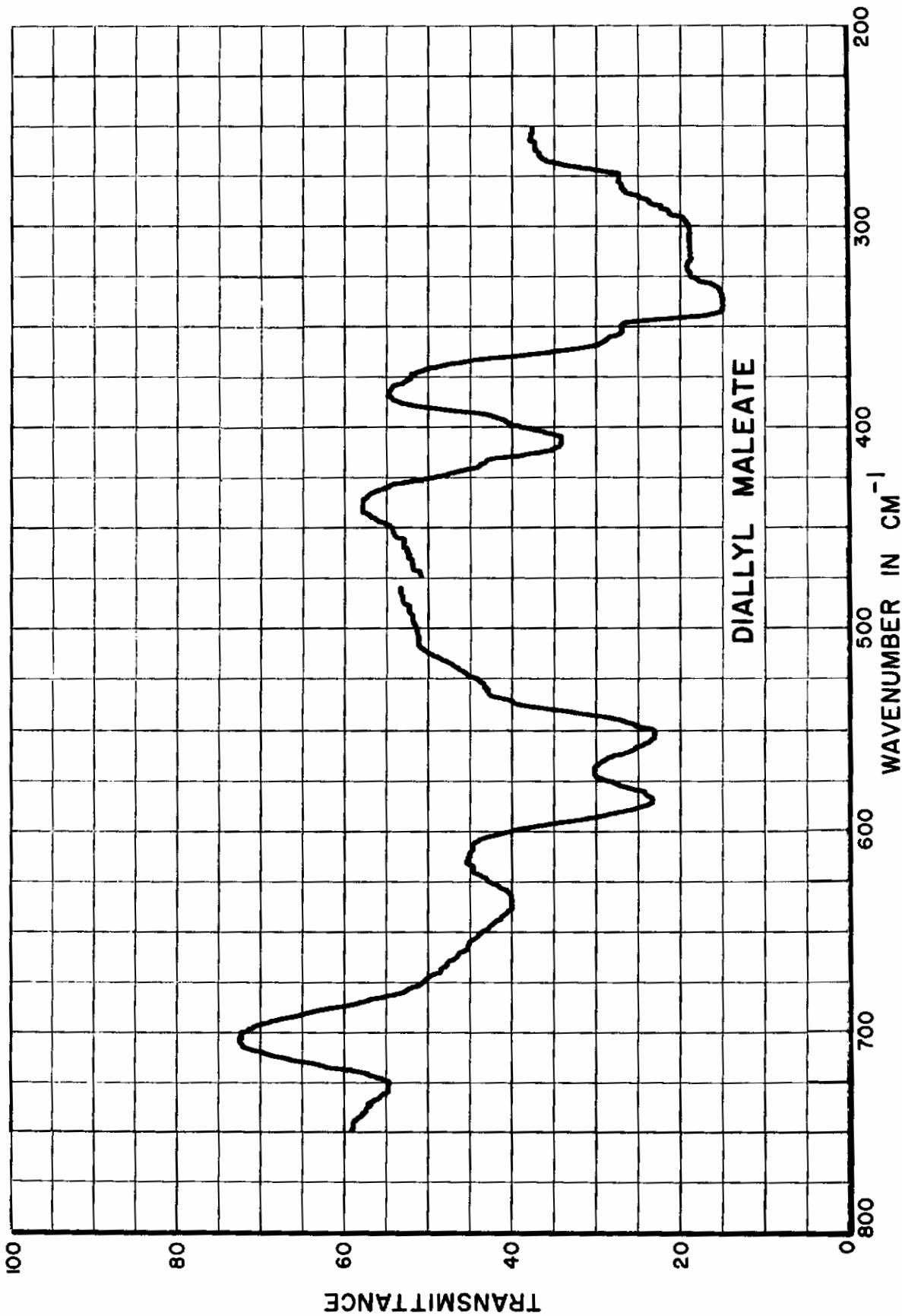


Figure 164. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Diallyl Maleate  
Recorded using a 0.21 mm CsBr cell

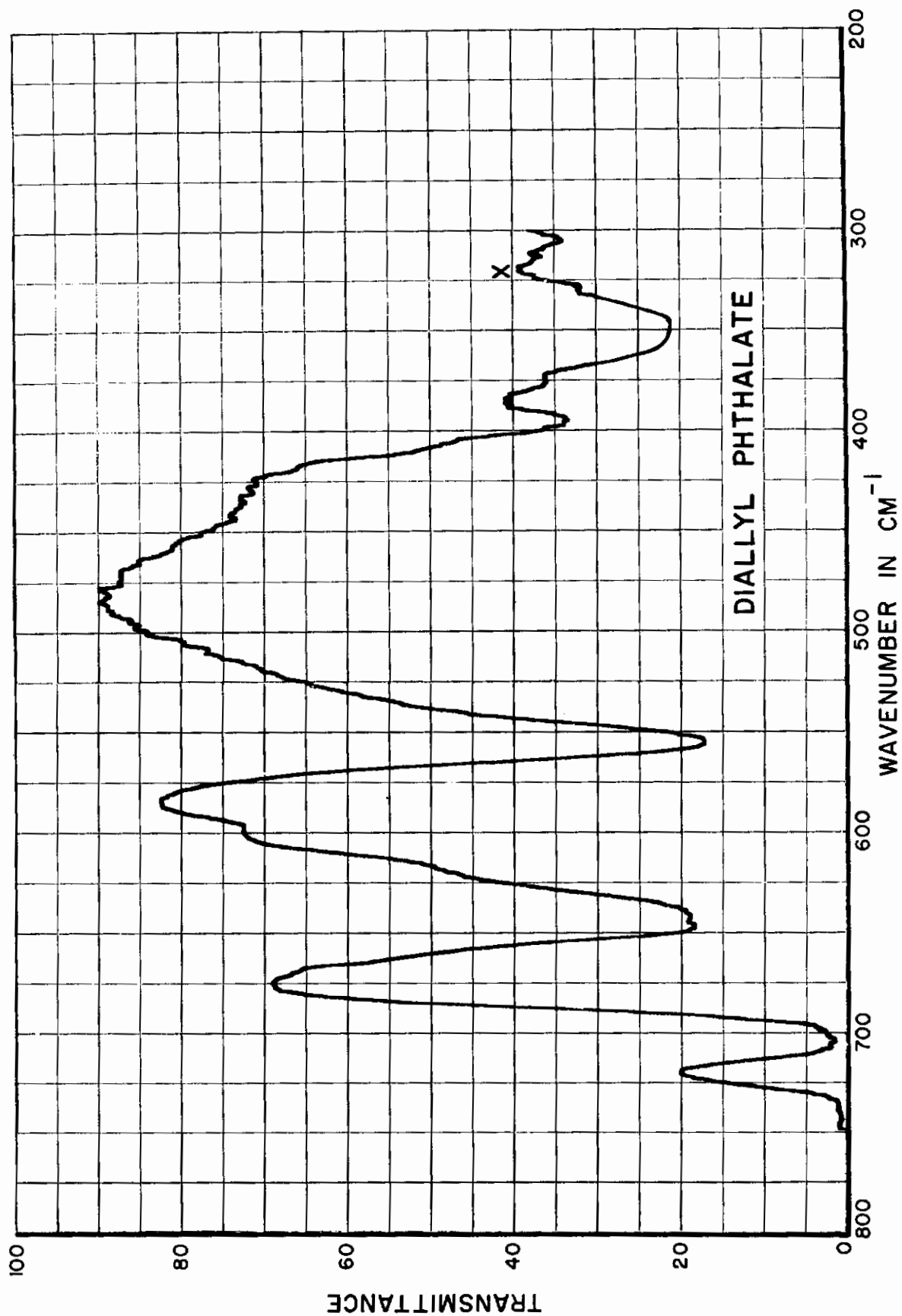


Figure 165. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of Diallyl Phthalate  
Recorded using a 0.21 mm CsBr cell

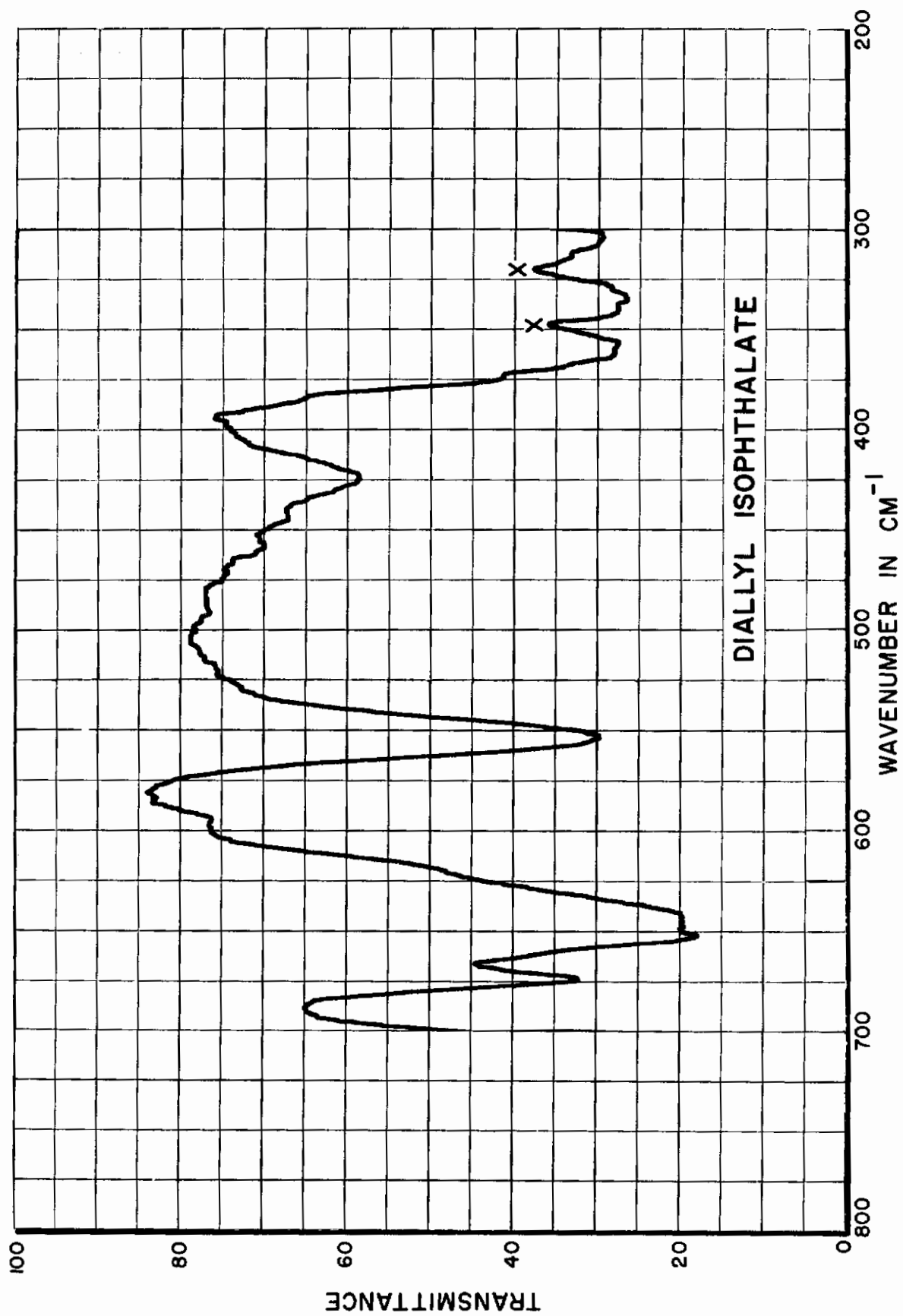


Figure 166. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Diallyl Isophthalate  
Recorded using a 0.1 mm CsBr cell



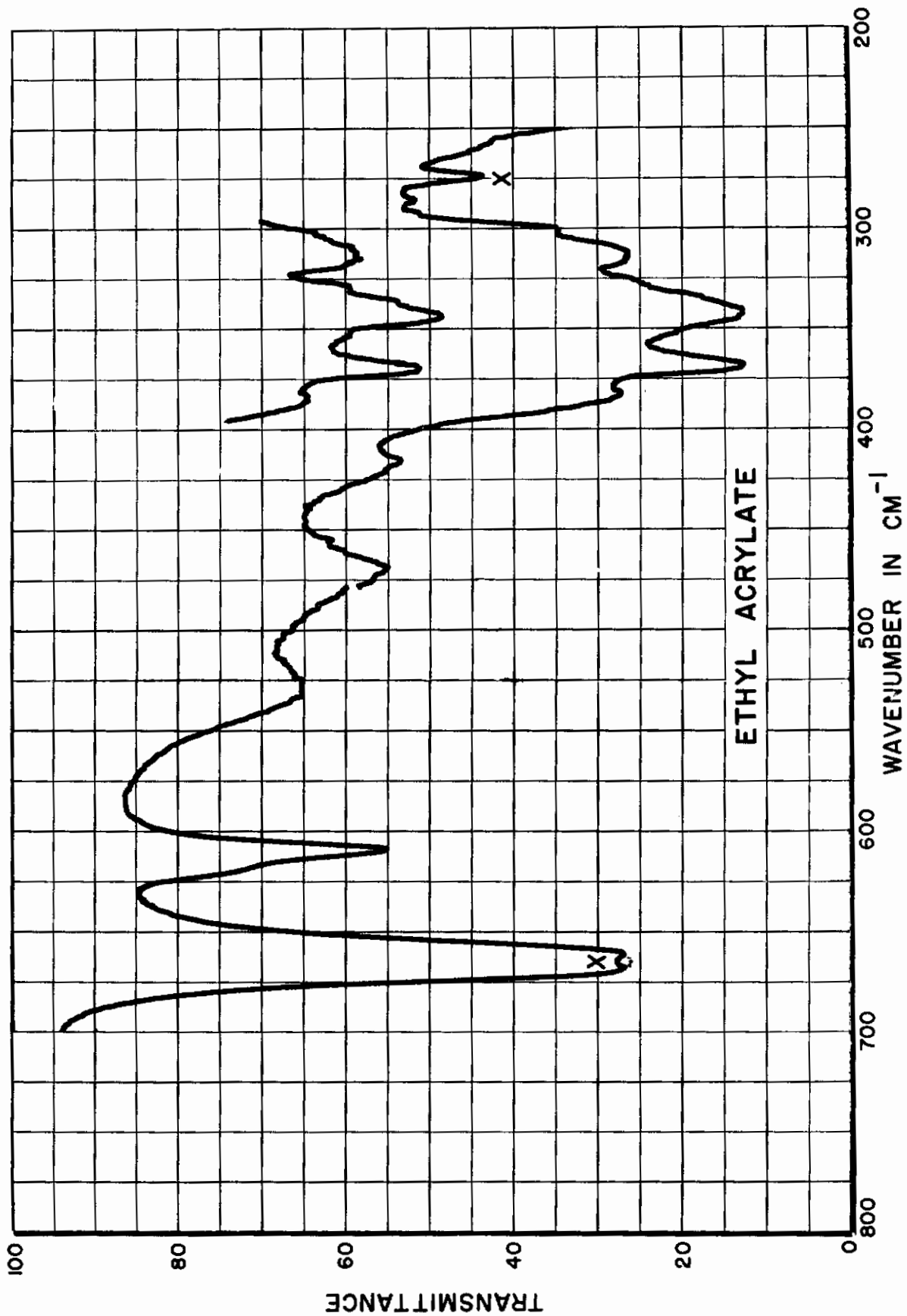


Figure 168. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Ethyl Acrylate  
Recorded using 0.1 and 0.02 mm CsBr cells

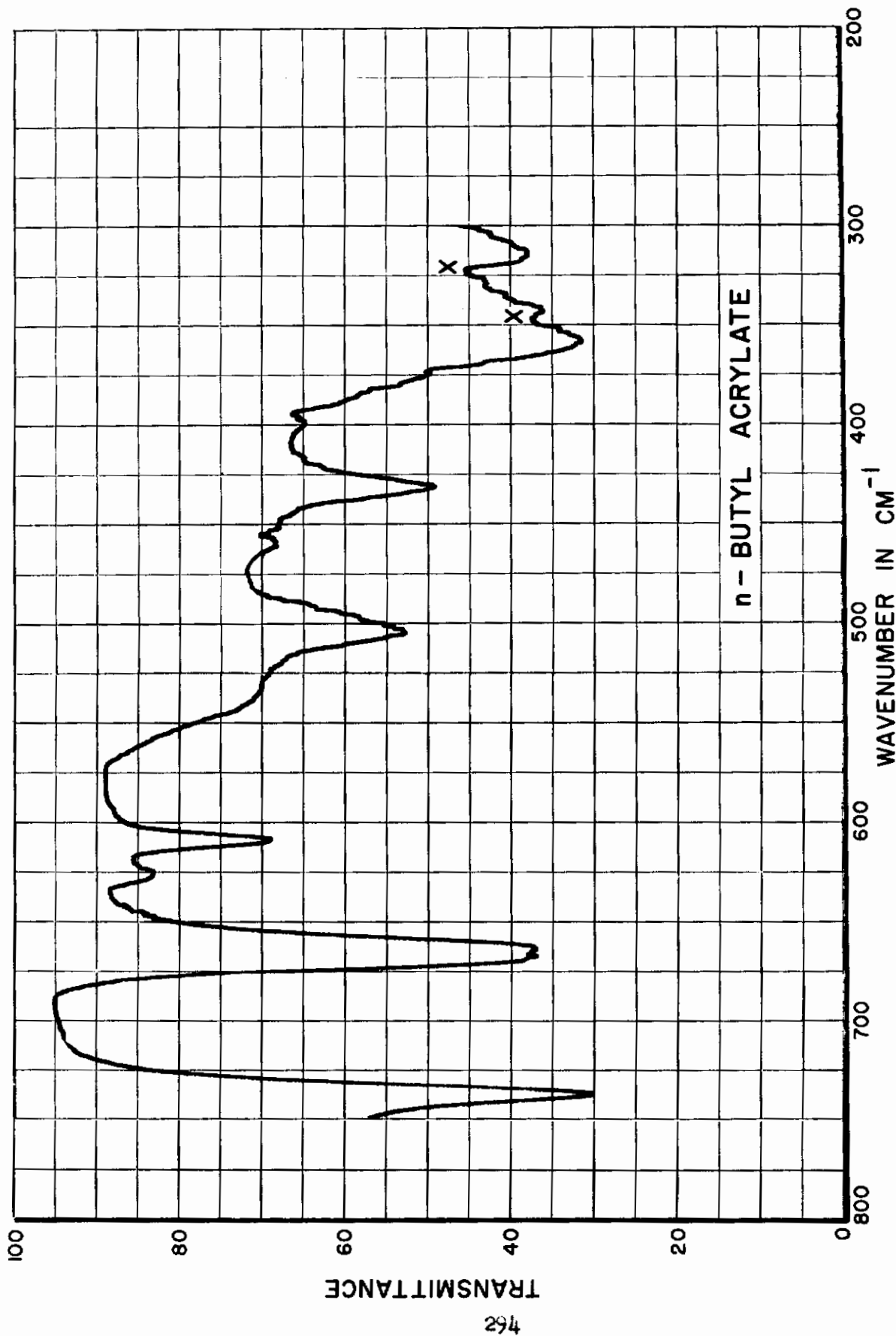


Figure 169. - Infrared Spectrum from 750 - 300 cm<sup>-1</sup> of n-Butyl Acrylate  
Recorded using a 0.1 mm CsBr cell

462

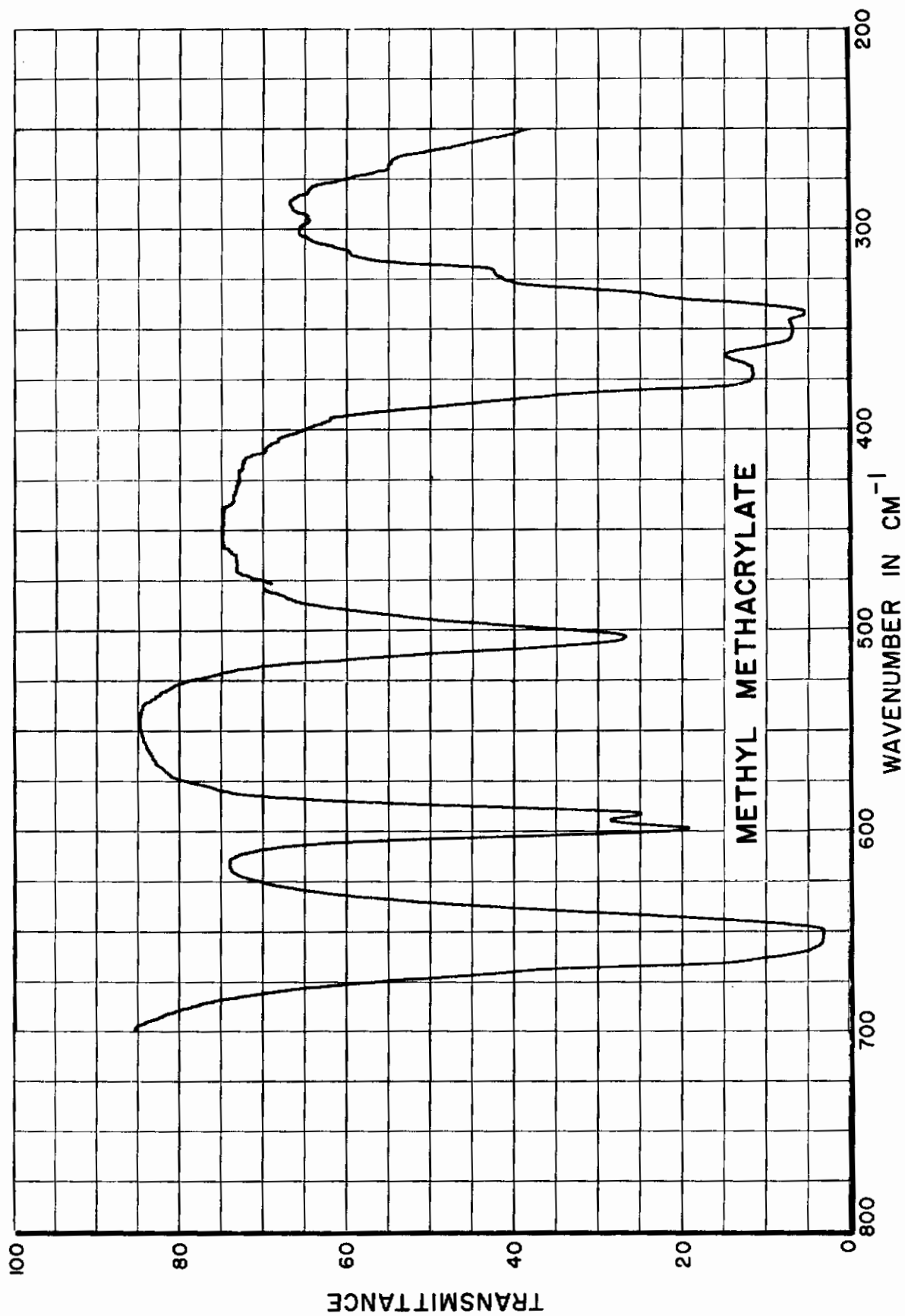


Figure 170. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Methyl Methacrylate  
Recorded using a 0.082 mm CsBr cell

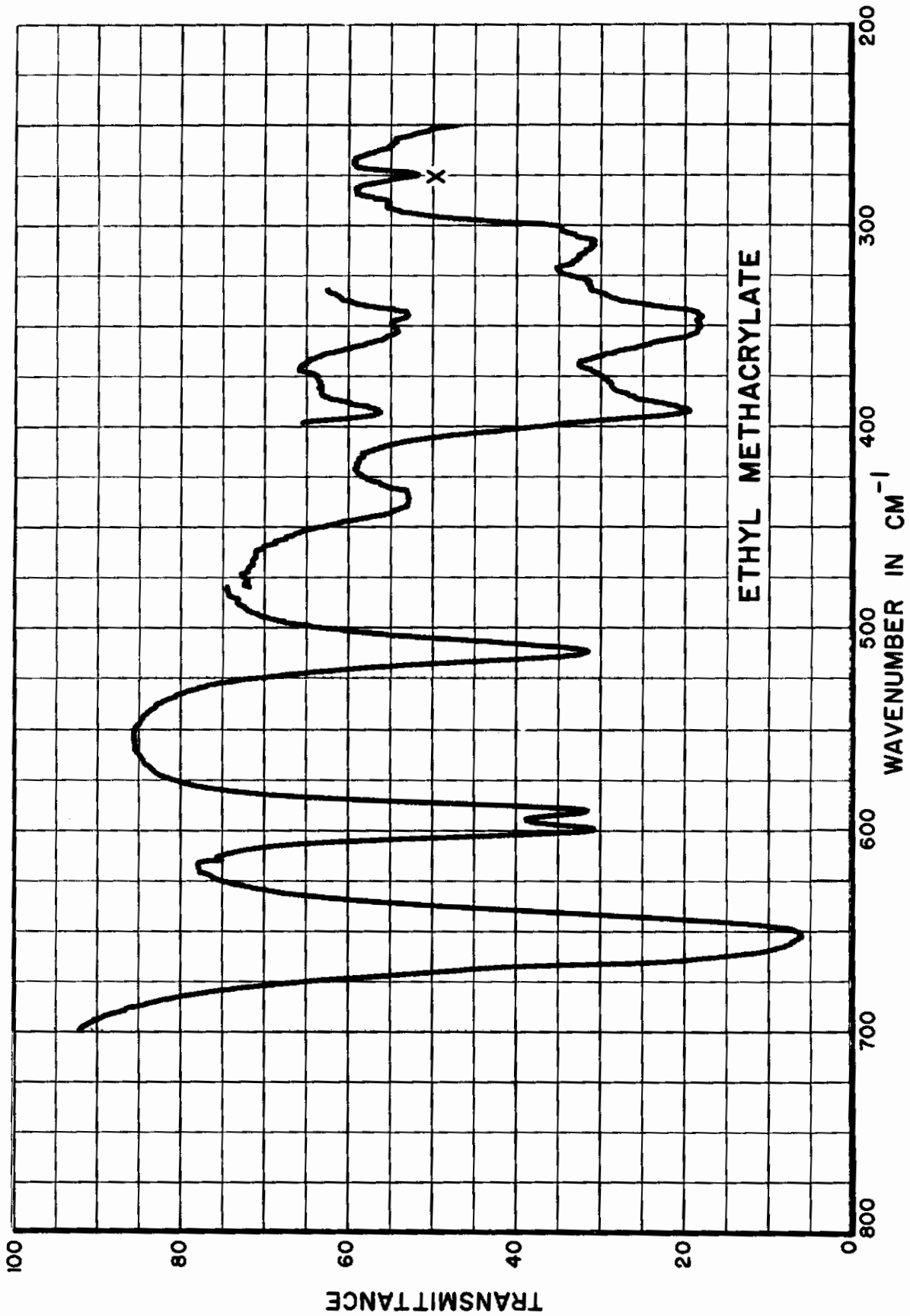


Figure 171. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Ethyl Methacrylate  
Recorded using 0.1 and 0.02 mm CsBr cells



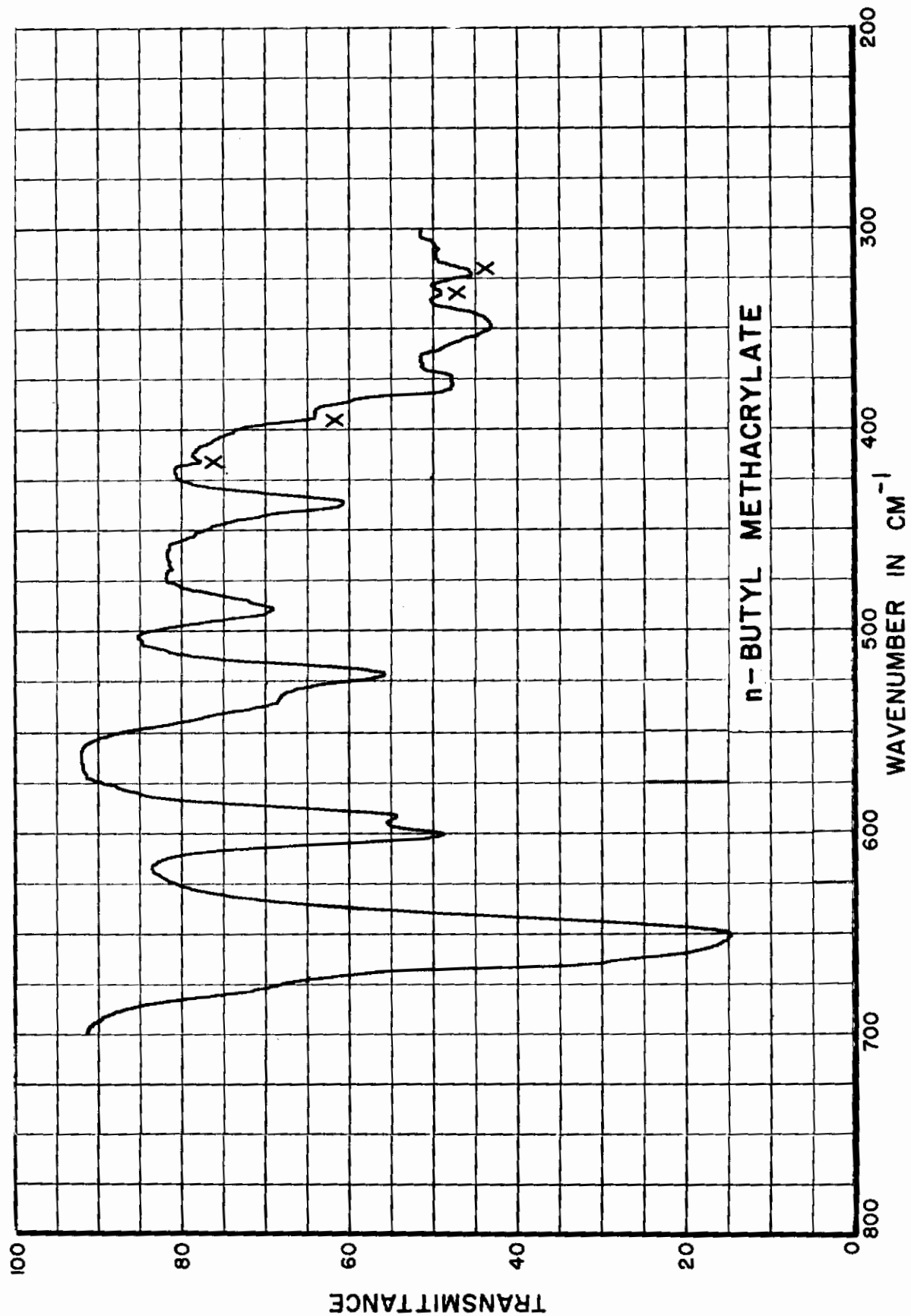


Figure 172. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of n-Butyl Methacrylate  
Recorded using a 0.1 mm CsBr cell

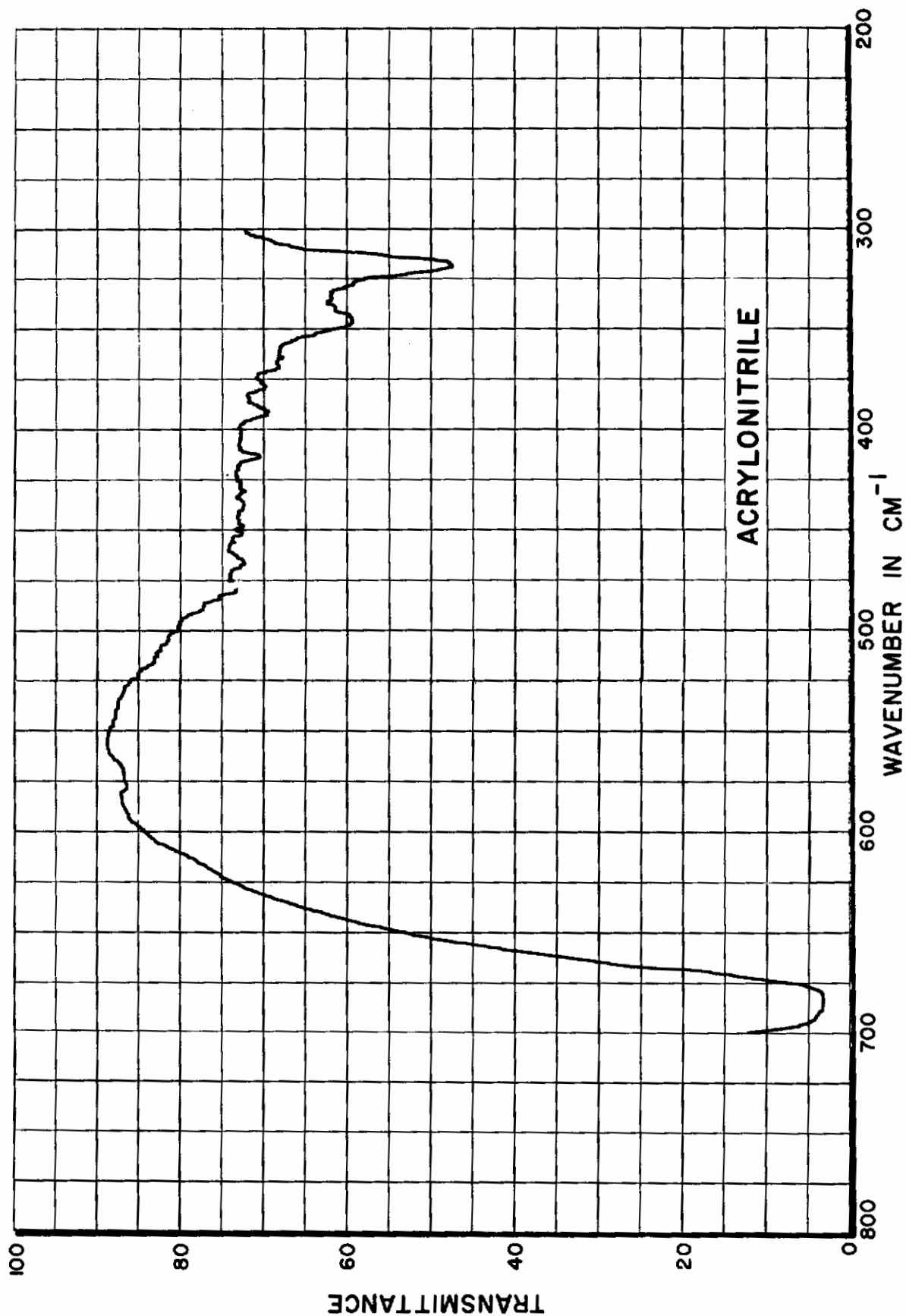


Figure 173. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Acrylonitrile  
Recorded using a 0.1 mm CsBr cell

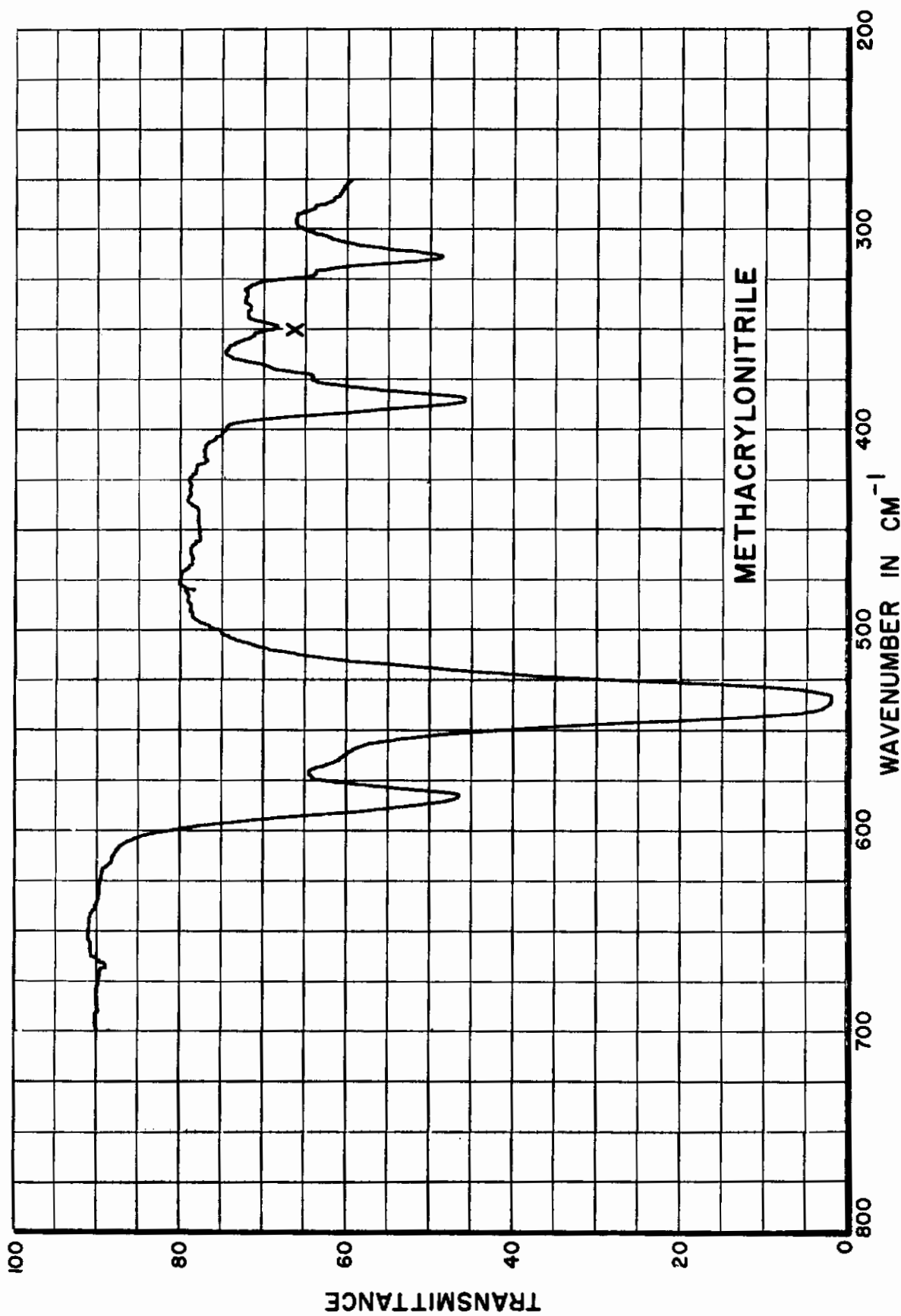


Figure 174. - Infrared Spectrum from 700 - 275 cm<sup>-1</sup> of Methacrylonitrile  
Recorded using a 0.1 mm CsBr cell

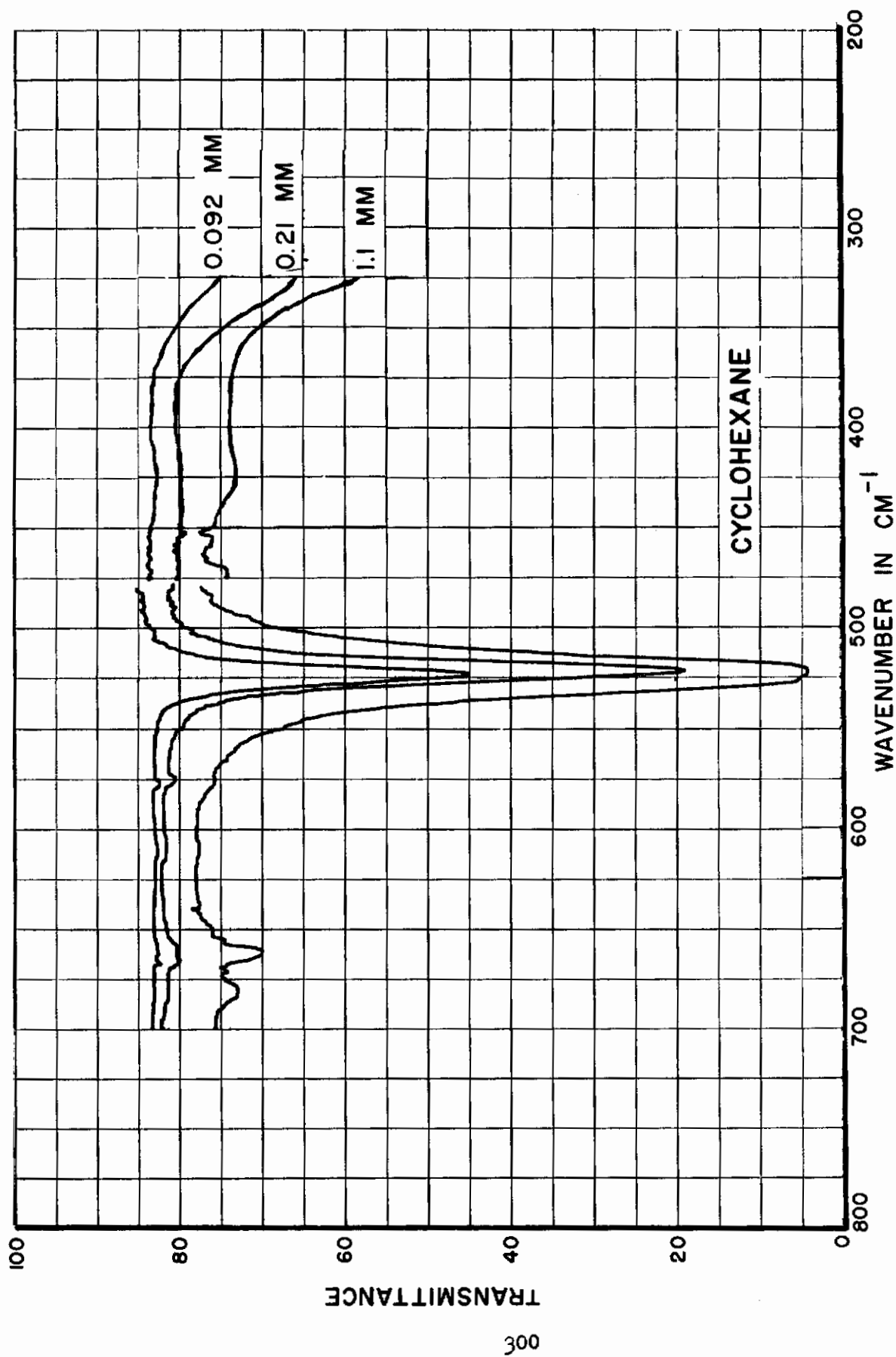


Figure 175. - Infrared Spectrum from 700 - 325 cm<sup>-1</sup> of Cyclohexane  
Recorded using 1.1, 0.21 and 0.092 mm. CsBr cells

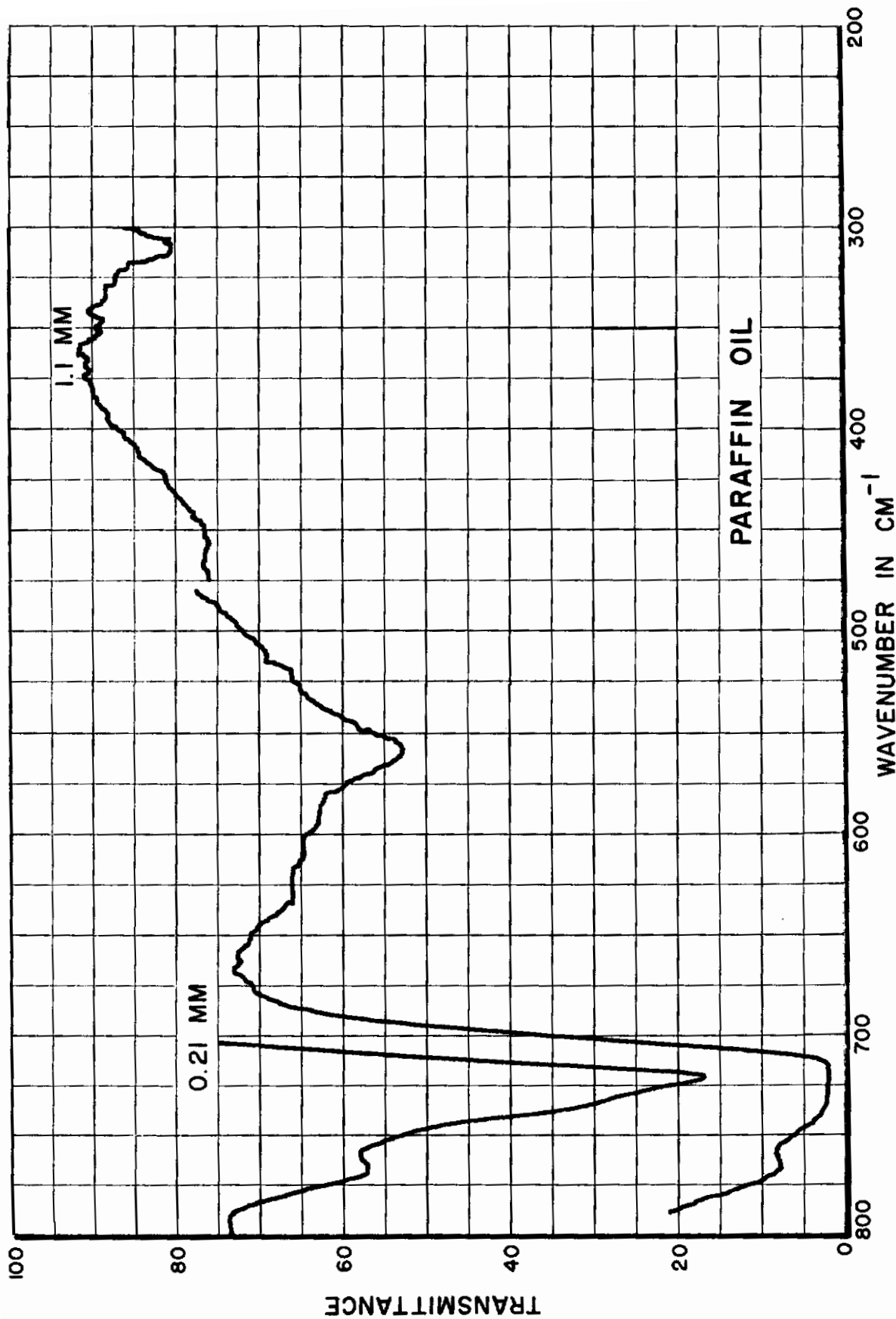


Figure 176. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Paraffin Oil (Nujol)  
Recorded using 1.1 and 0.21 mm CsBr cells

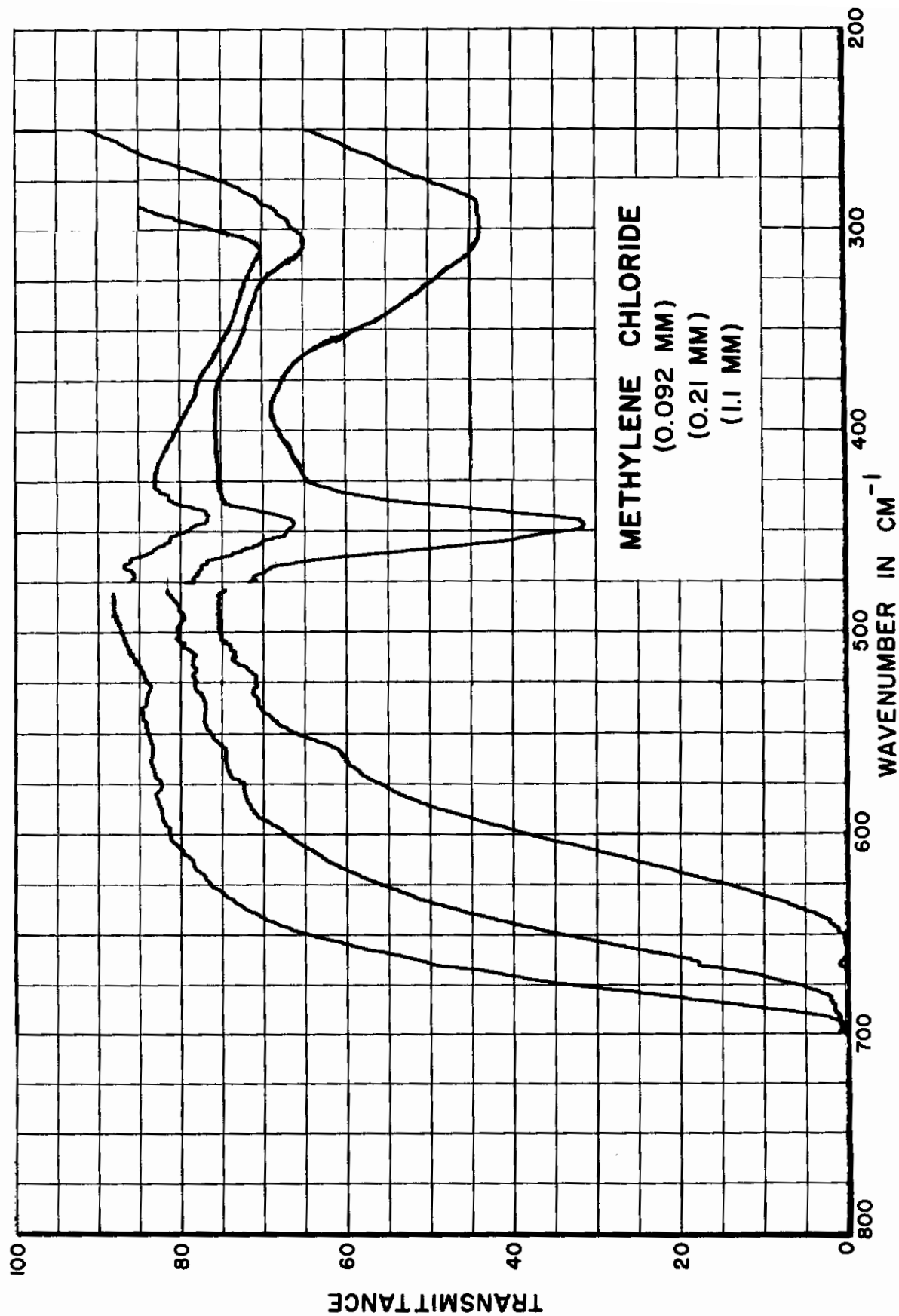


Figure 177. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of Methylene Chloride  
Recorded using 1.1, 0.21 and 0.092 mm CsBr cells

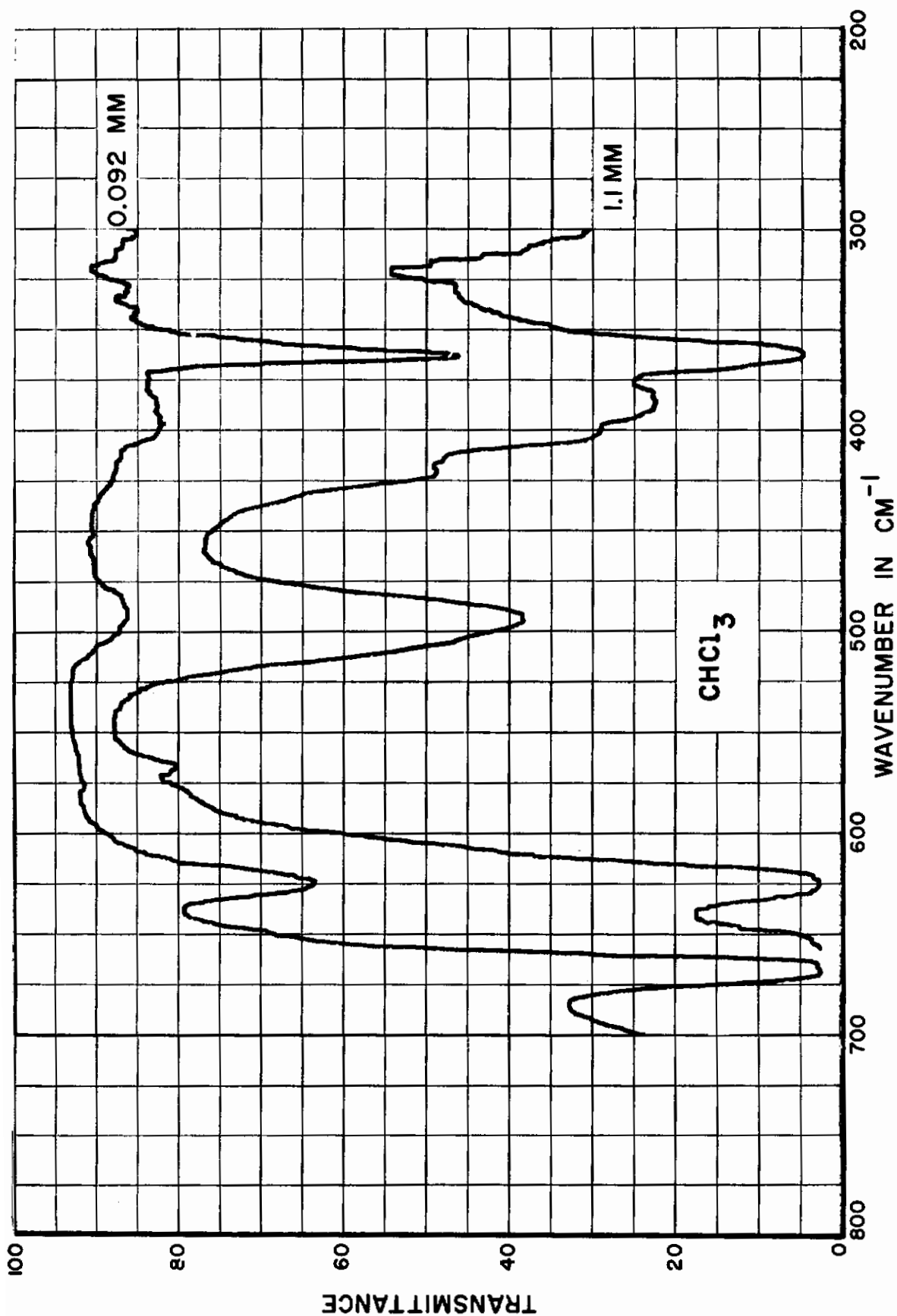


Figure 178. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Chloroform  
Recorded using 1.1 and 0.092 mm CsBr cells

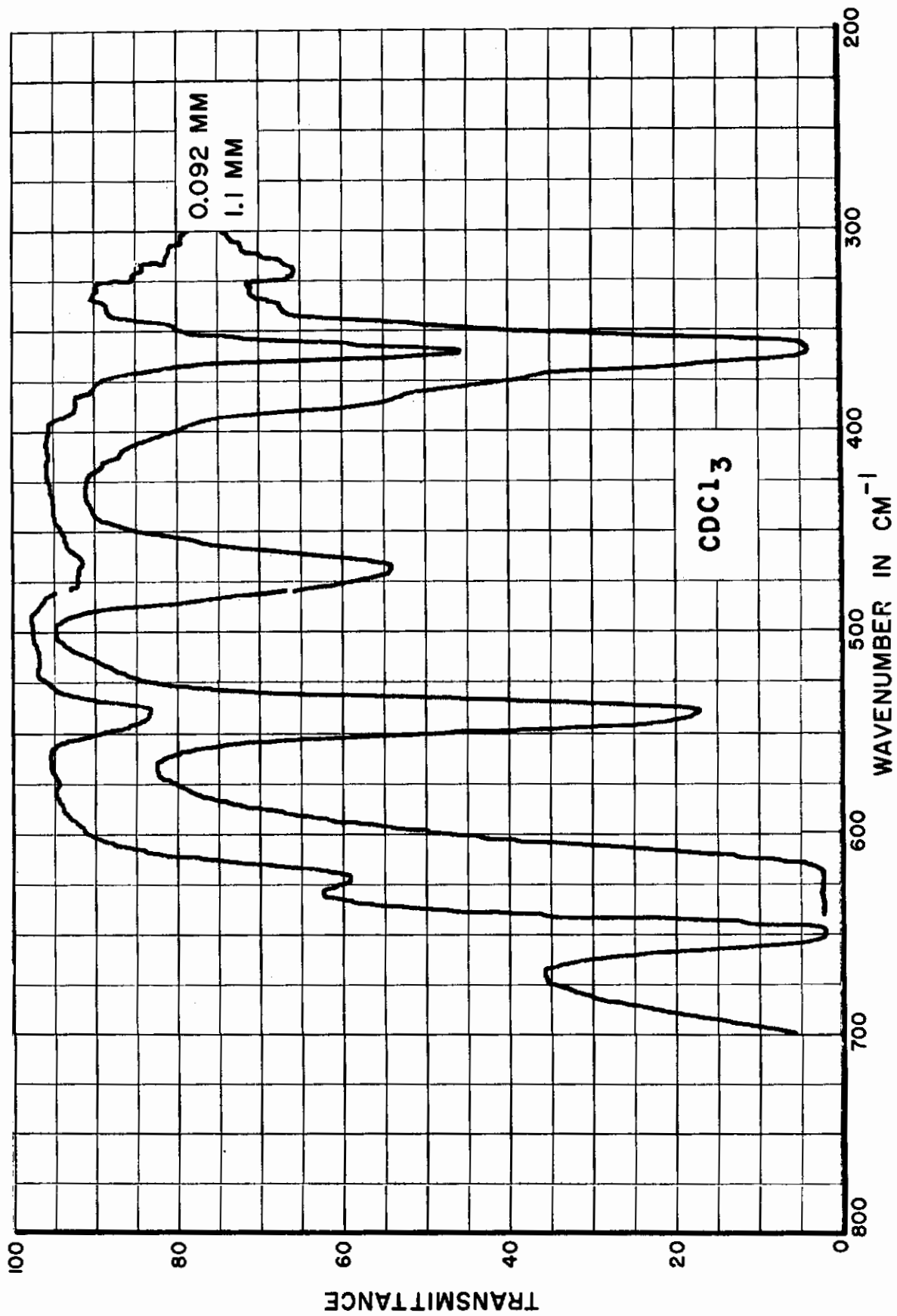


Figure 179. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Deuterated Chloroform  
Recorded using 1.1 and 0.092 mm CsBr cells



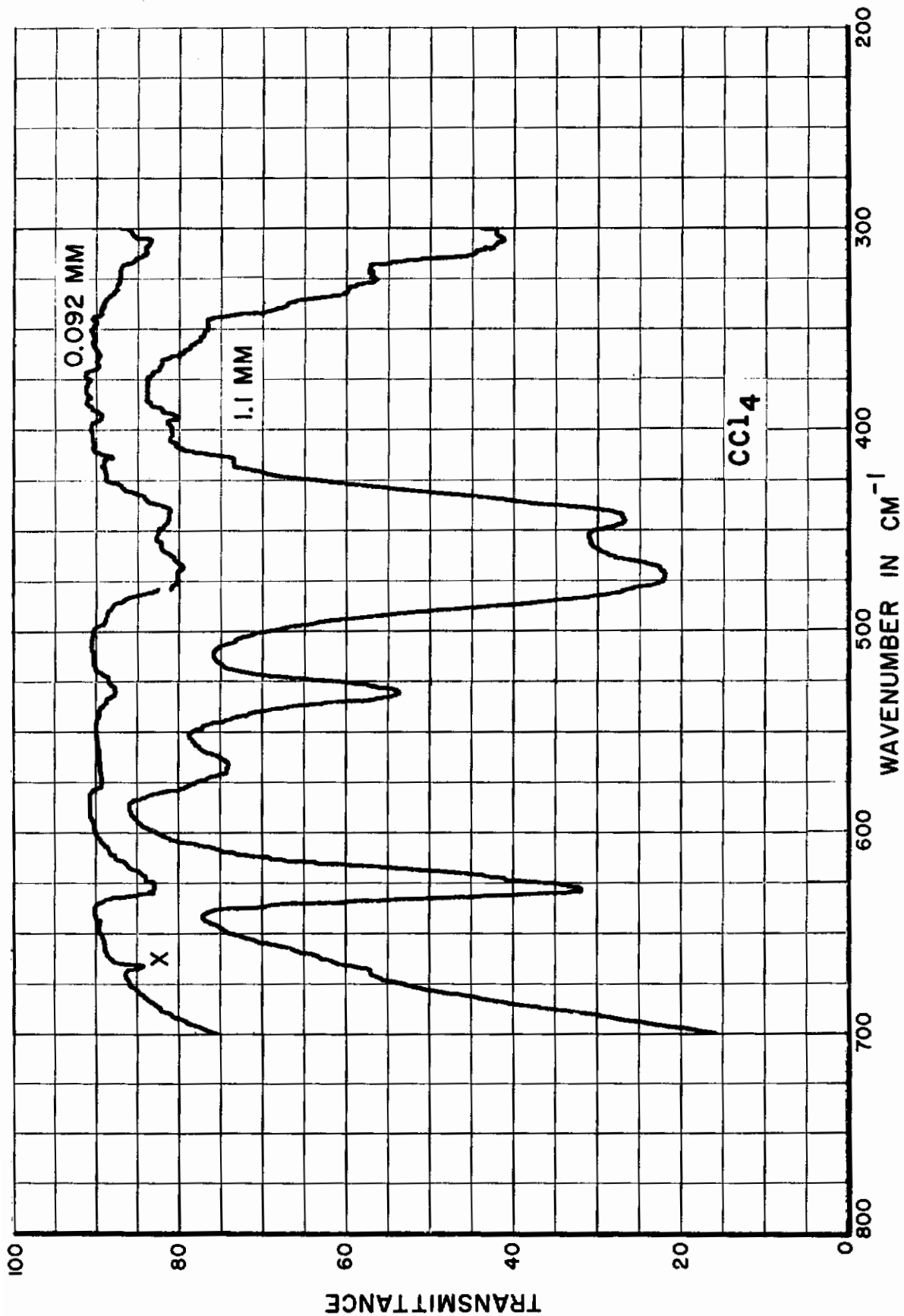


Figure 180. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Carbon Tetrachloride  
Recorded using 1.1 and 0.092 mm CsBr cells

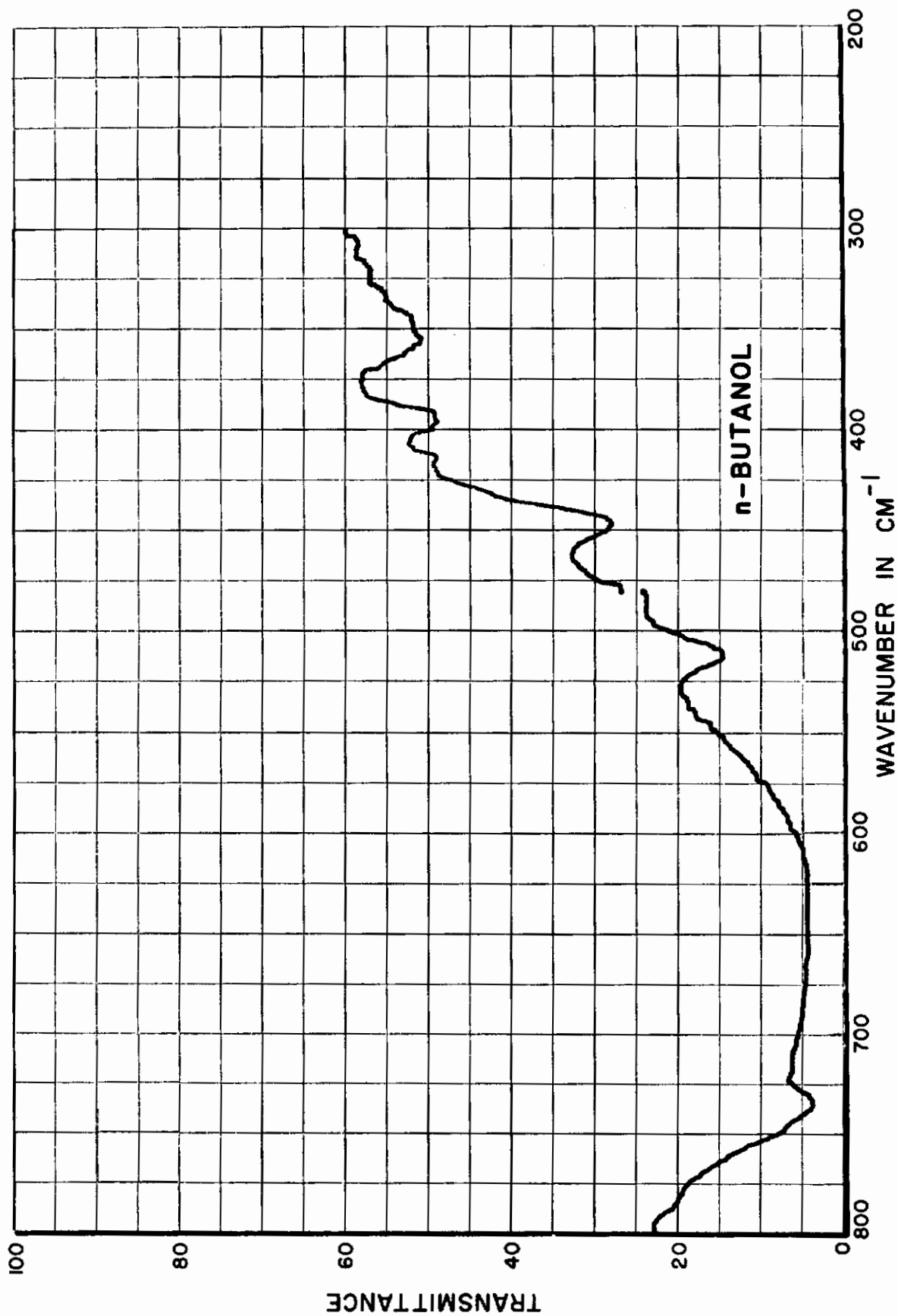


Figure 181. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of n-Butanol  
Recorded using a 0.092 mm CsBr cell

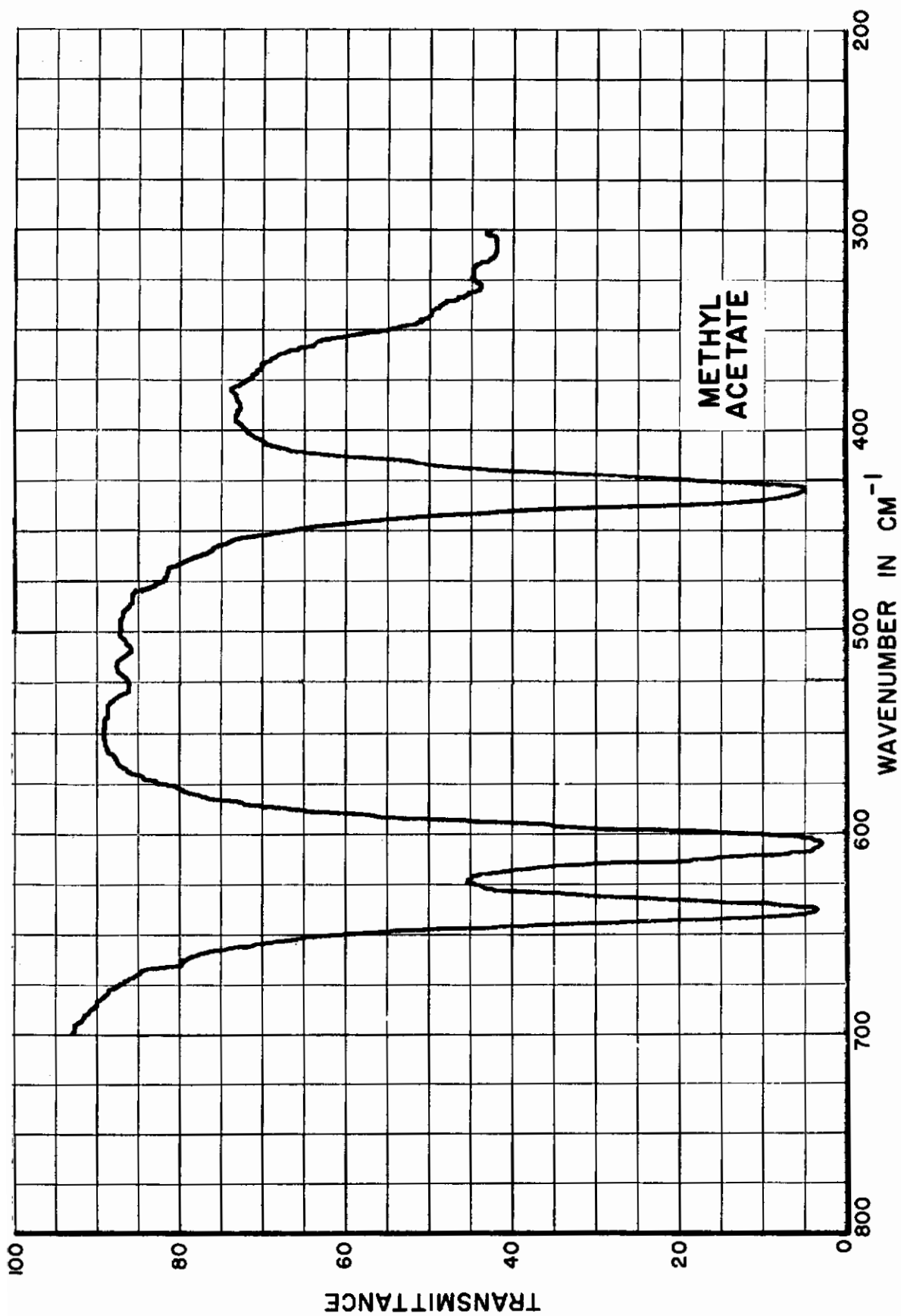


Figure 182. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Methyl Acetate  
Recorded using a 0.092 mm CsBr cell

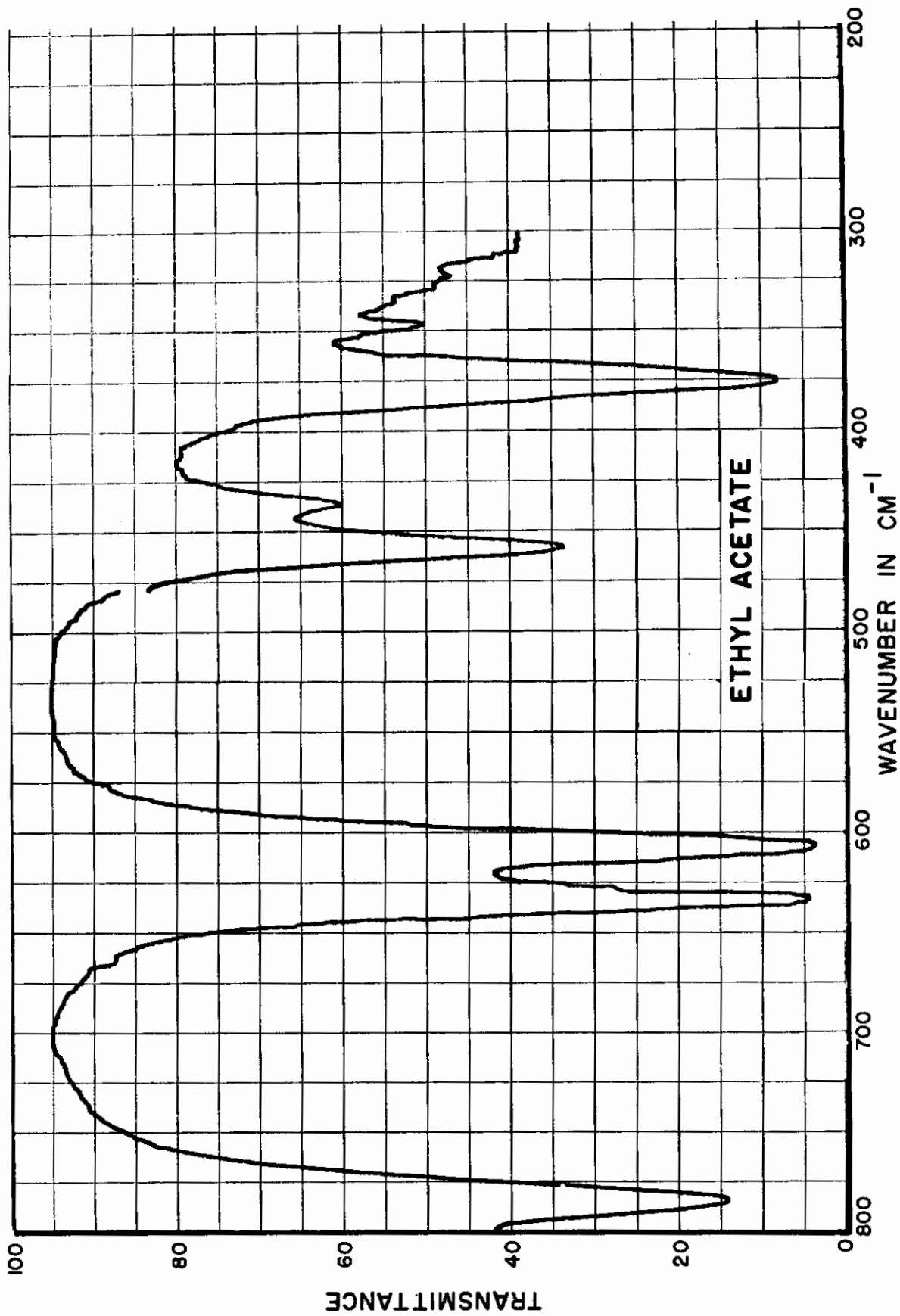


Figure 183. - Infrared Spectrum from 800 - 300 cm<sup>-1</sup> of Ethyl Acetate  
Recorded using a 0.092 mm CsBr cell

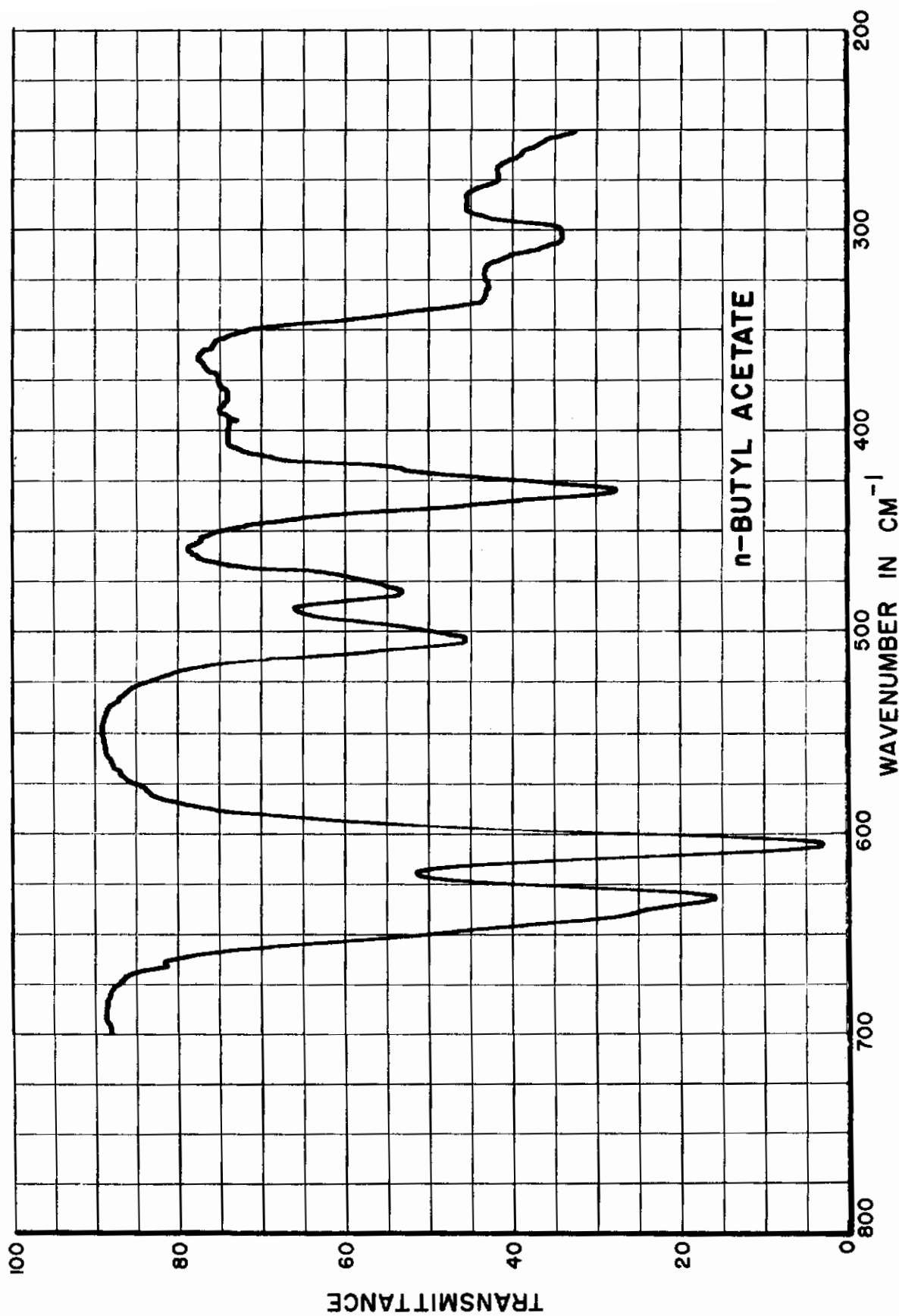


Figure 184. - Infrared Spectrum from 700 - 250 cm<sup>-1</sup> of n-Butyl Acetate  
Recorded using a 0.092 mm CsBr cell

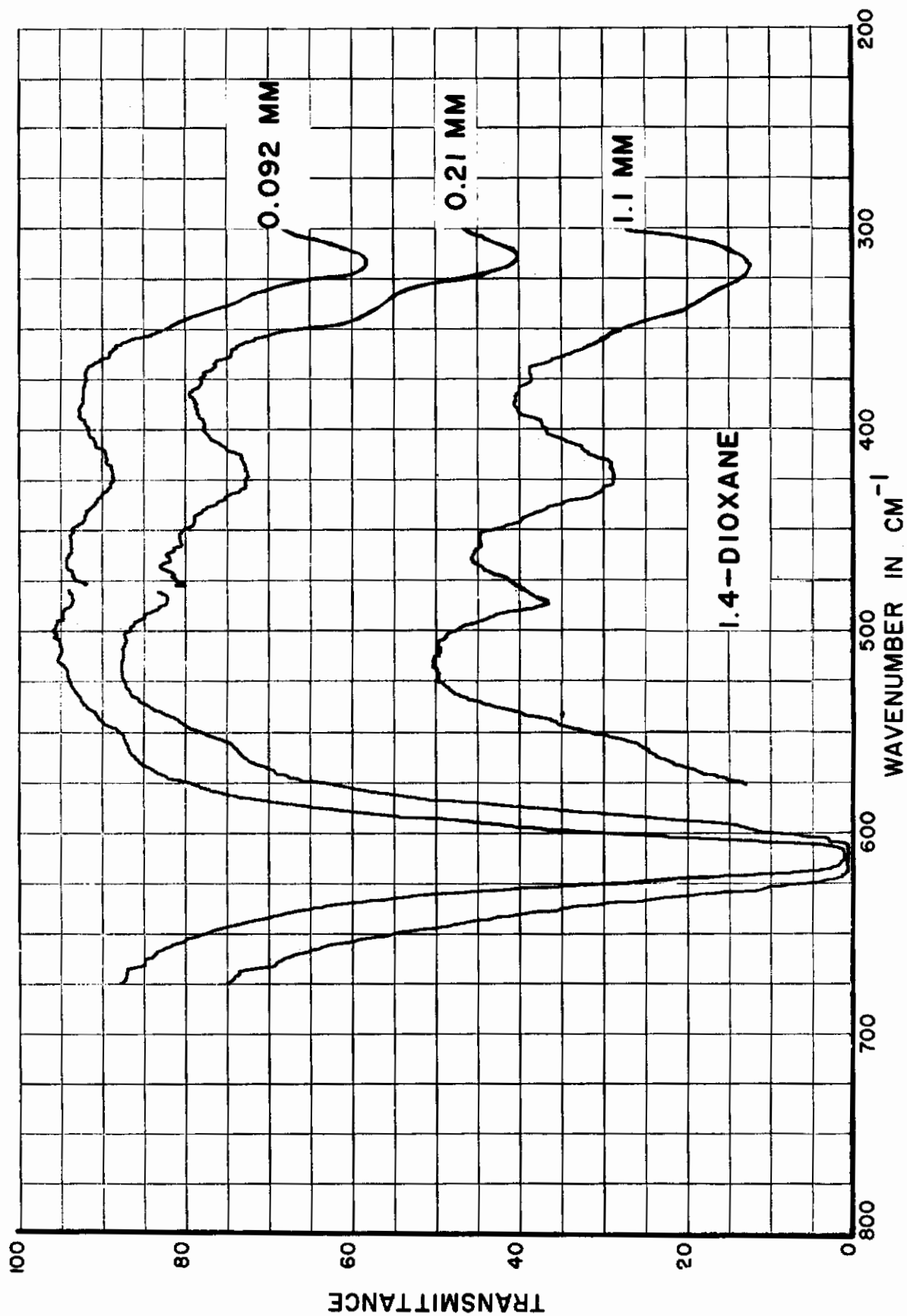


Figure 185. - Infrared Spectrum from 675 - 300 cm<sup>-1</sup> of 1,4-Dioxane  
Recorded using 1.1, 0.21, 0.092 mm CsBr cells

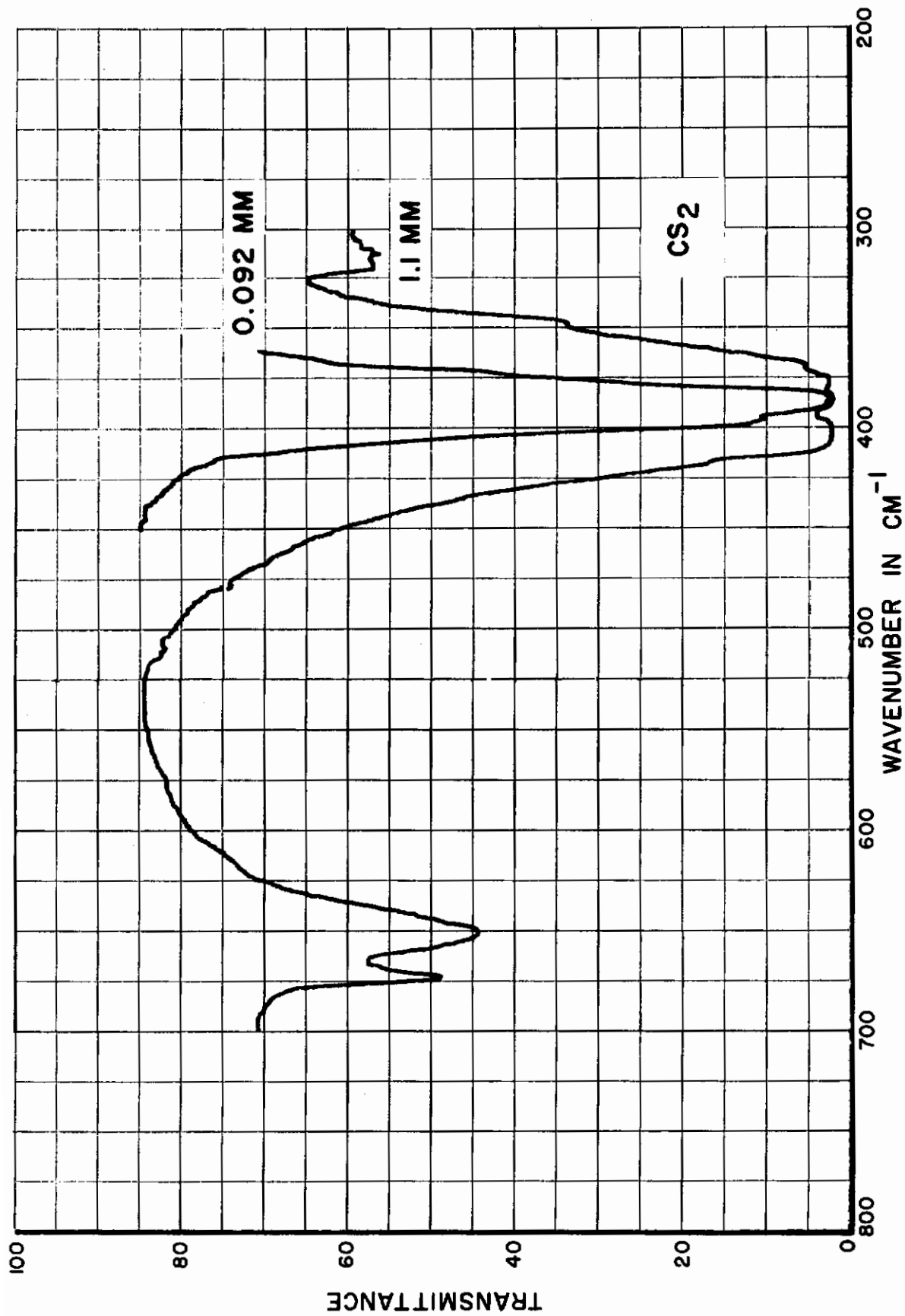


Figure 186. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Carbon Disulfide  
Recorded using 1.1 and 0.092 mm CsBr cells

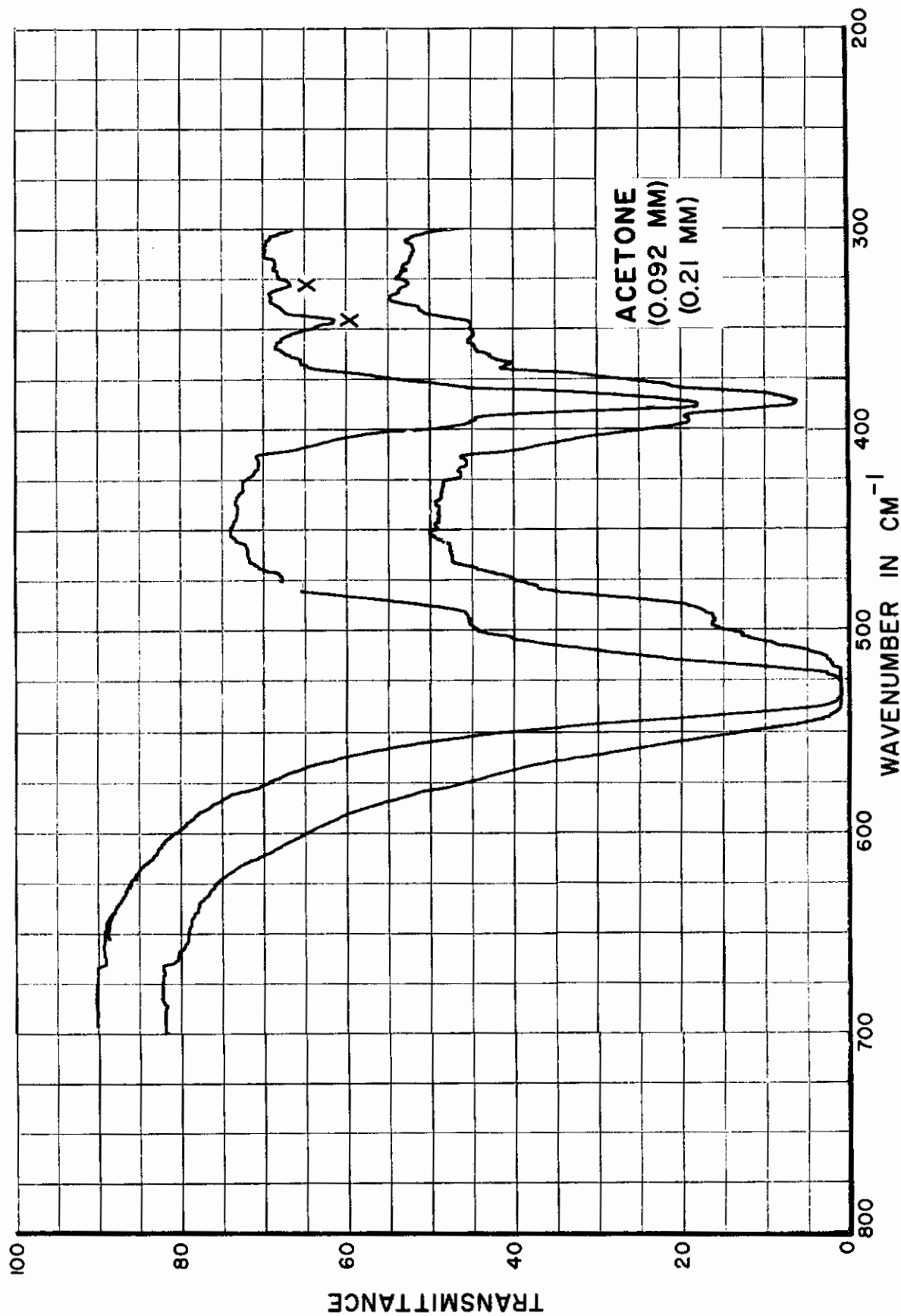


Figure 187. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Acetone  
Recorded using 0.21 and 0.092 mm CsBr cells



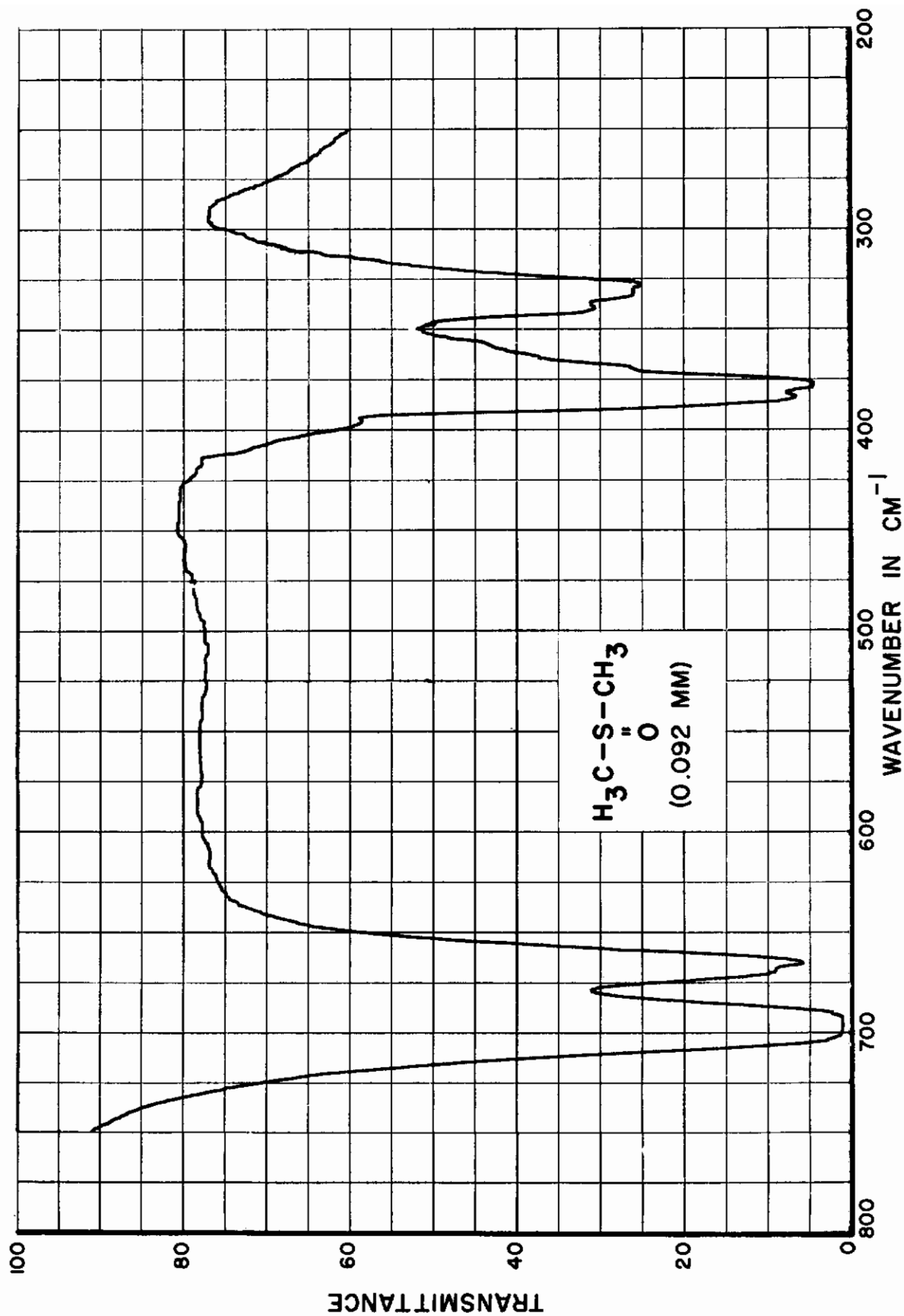


Figure 188. - Infrared Spectrum from 750 - 250 cm<sup>-1</sup> of Dimethyl Sulfoxide  
Recorded using a 0.092 mm CsBr cell

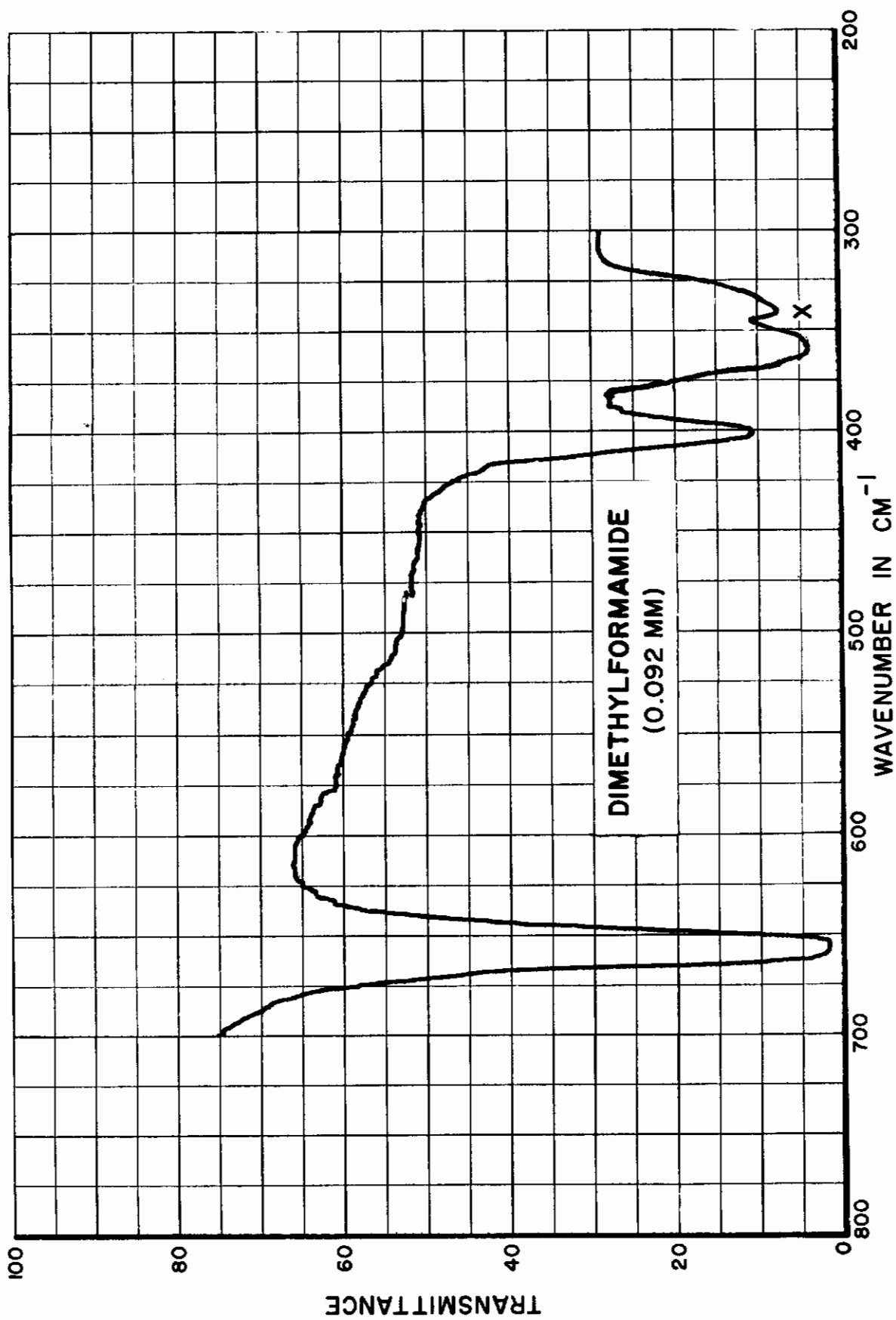


Figure 189. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Dimethylformamide  
Recorded using a 0.092 mm CsBr cell

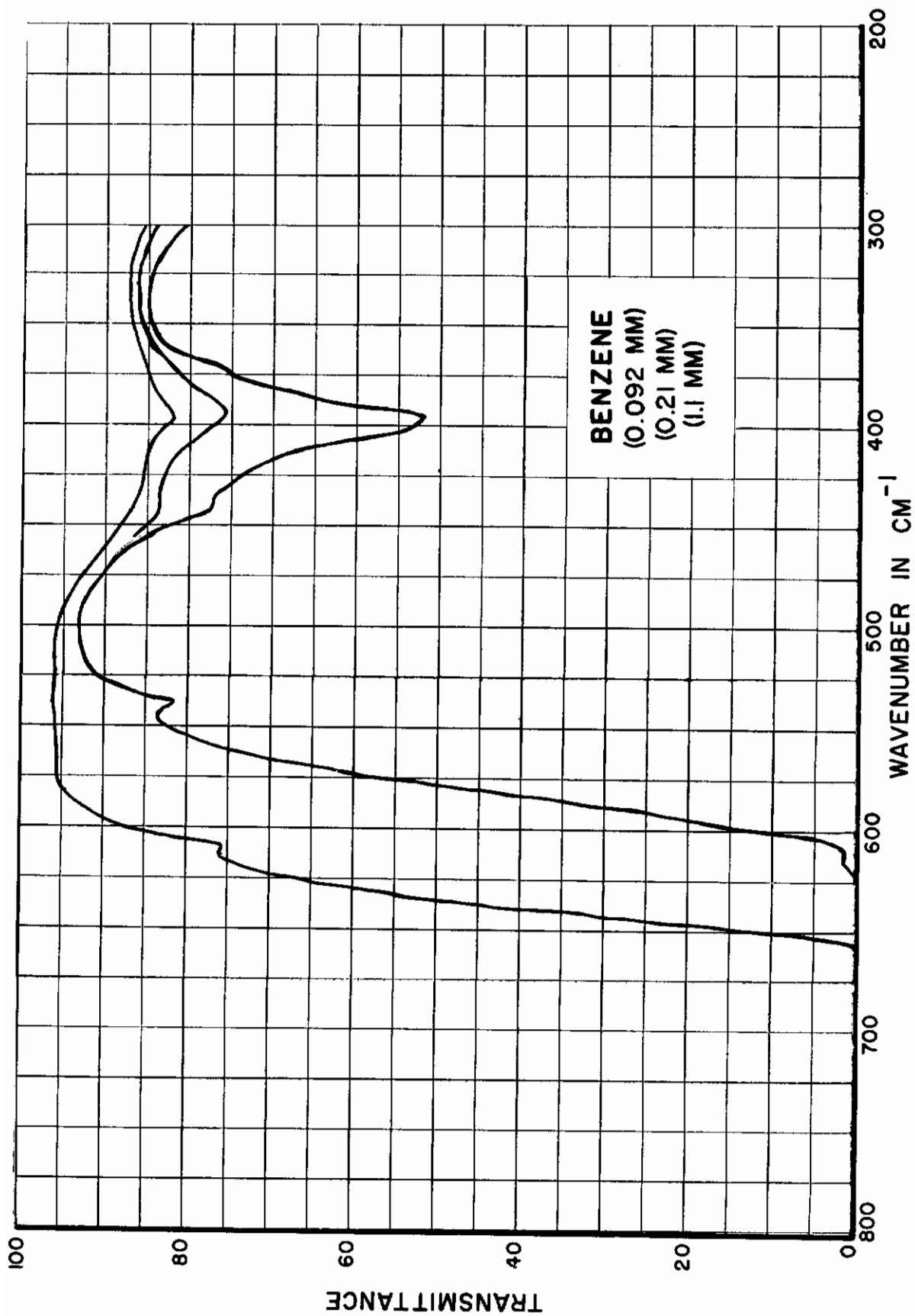


Figure 190. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Benzene  
Recorded using 1.1, 0.21 and 0.092 mm CsBr cells

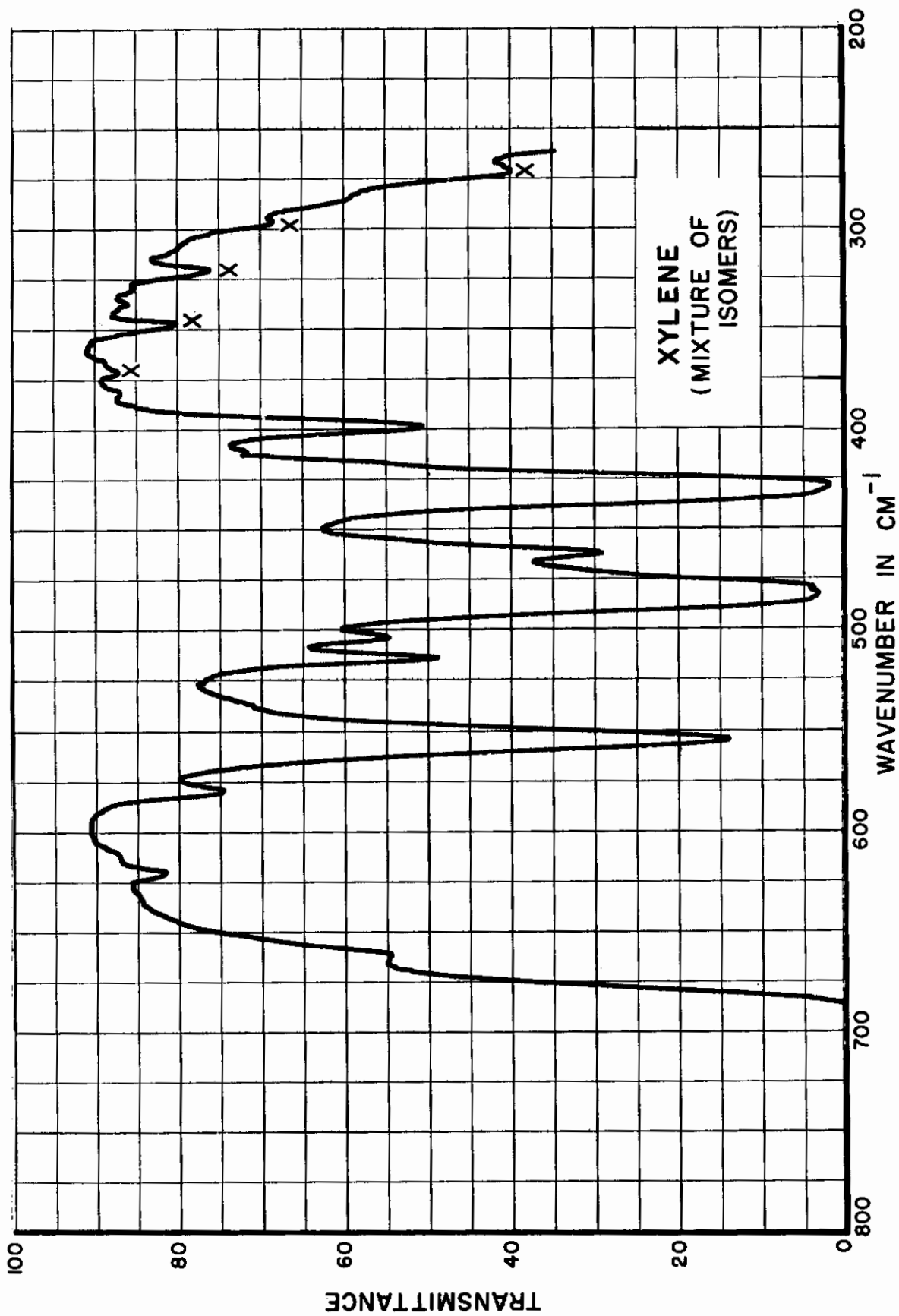


Figure 191. - Infrared Spectrum from 700 - 275 cm<sup>-1</sup> of Xylene (Mixture of Isomers)  
Recorded using a 0.092 mm CsBr cell

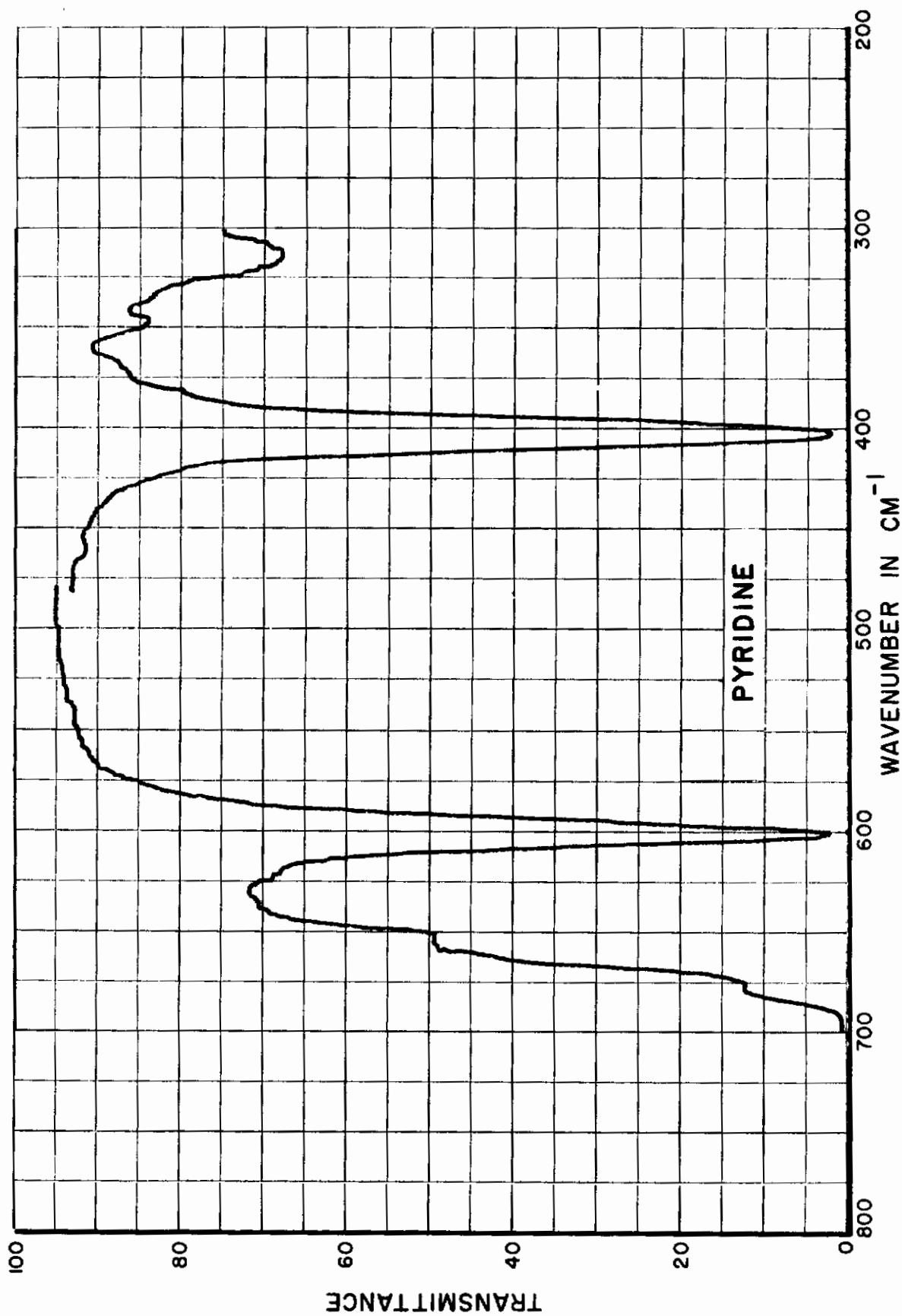


Figure 192. - Infrared Spectrum from 700 - 300 cm<sup>-1</sup> of Pyridine  
Recorded using a 0.092 mm CsBr cell

# *Contrails*

APPENDIX B

PICTORIAL SPECTRAL CHARTS OF  
POLYMERS, RESINS, AND  
RELATED MATERIALS.

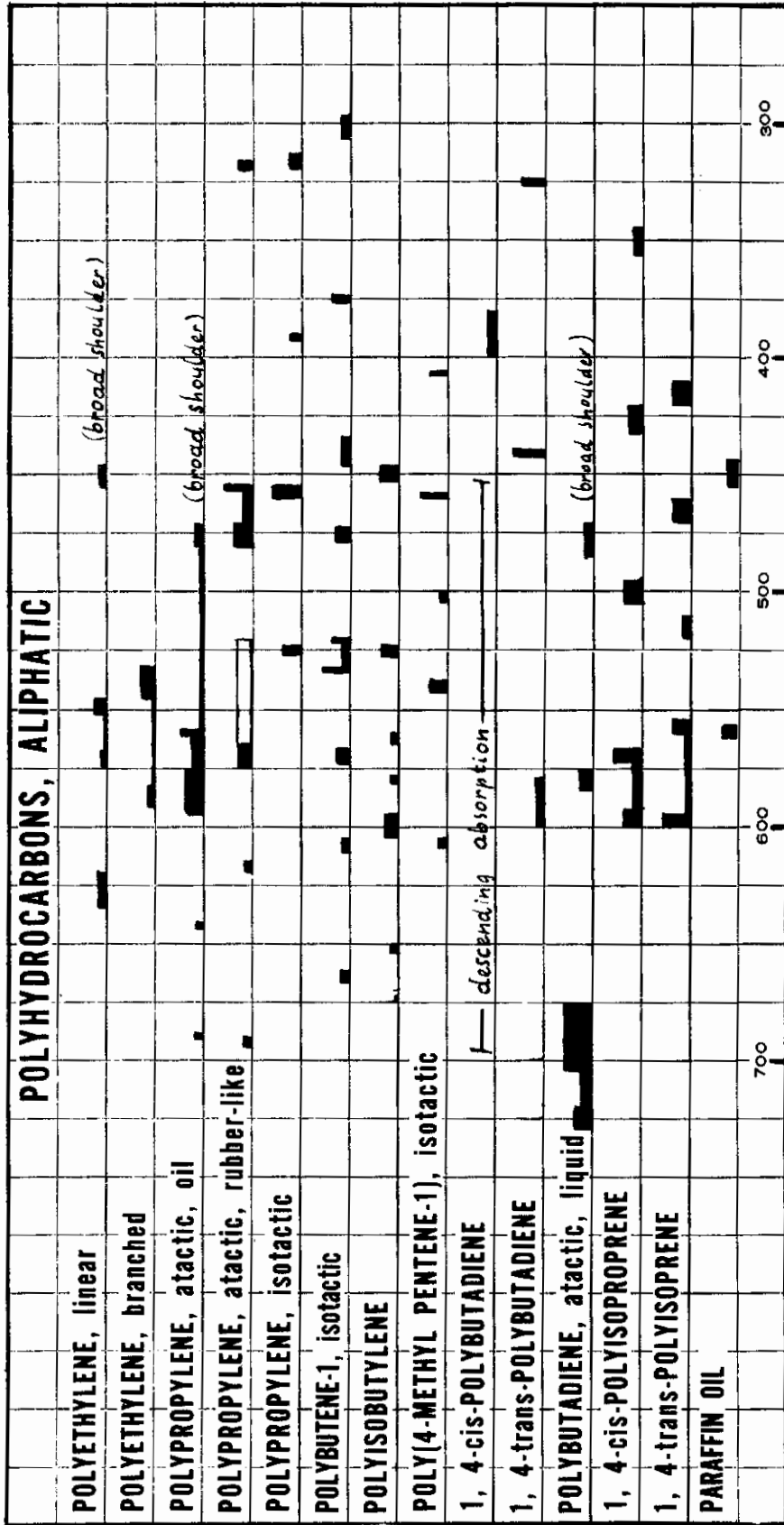


Chart I. - Absorption Frequencies of Aliphatic Polyhydrocarbons



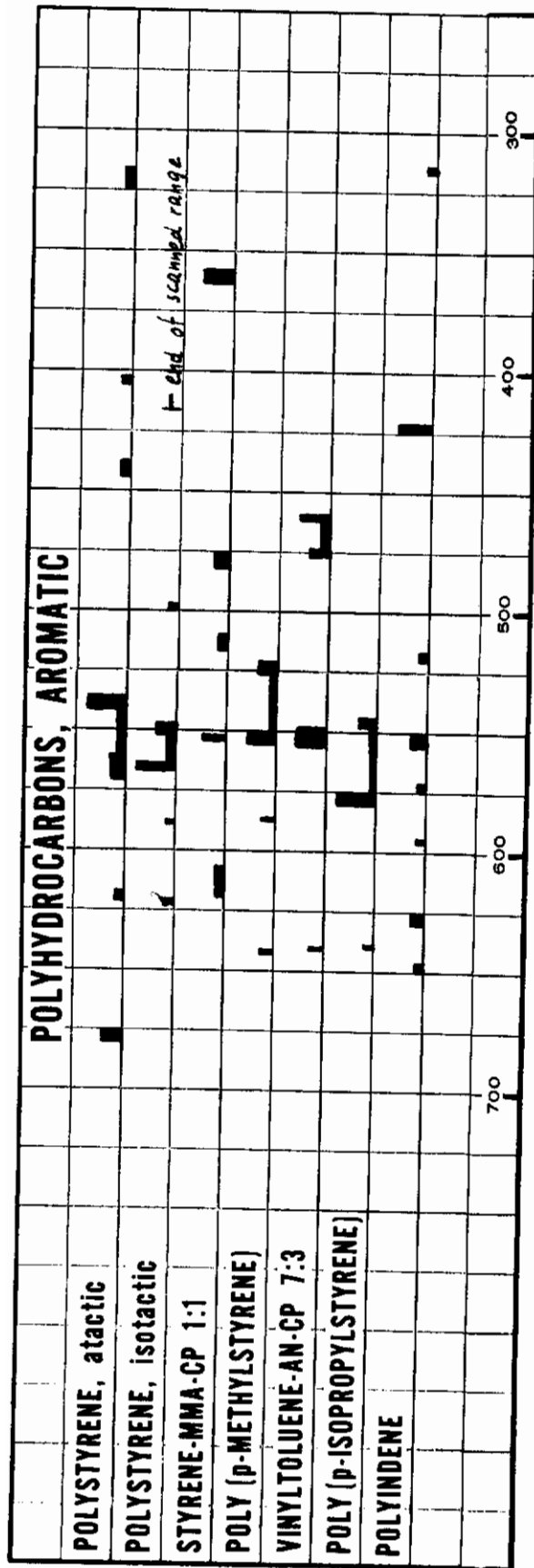


Chart II. - Absorption Frequencies of Aromatic Polyhydrocarbons

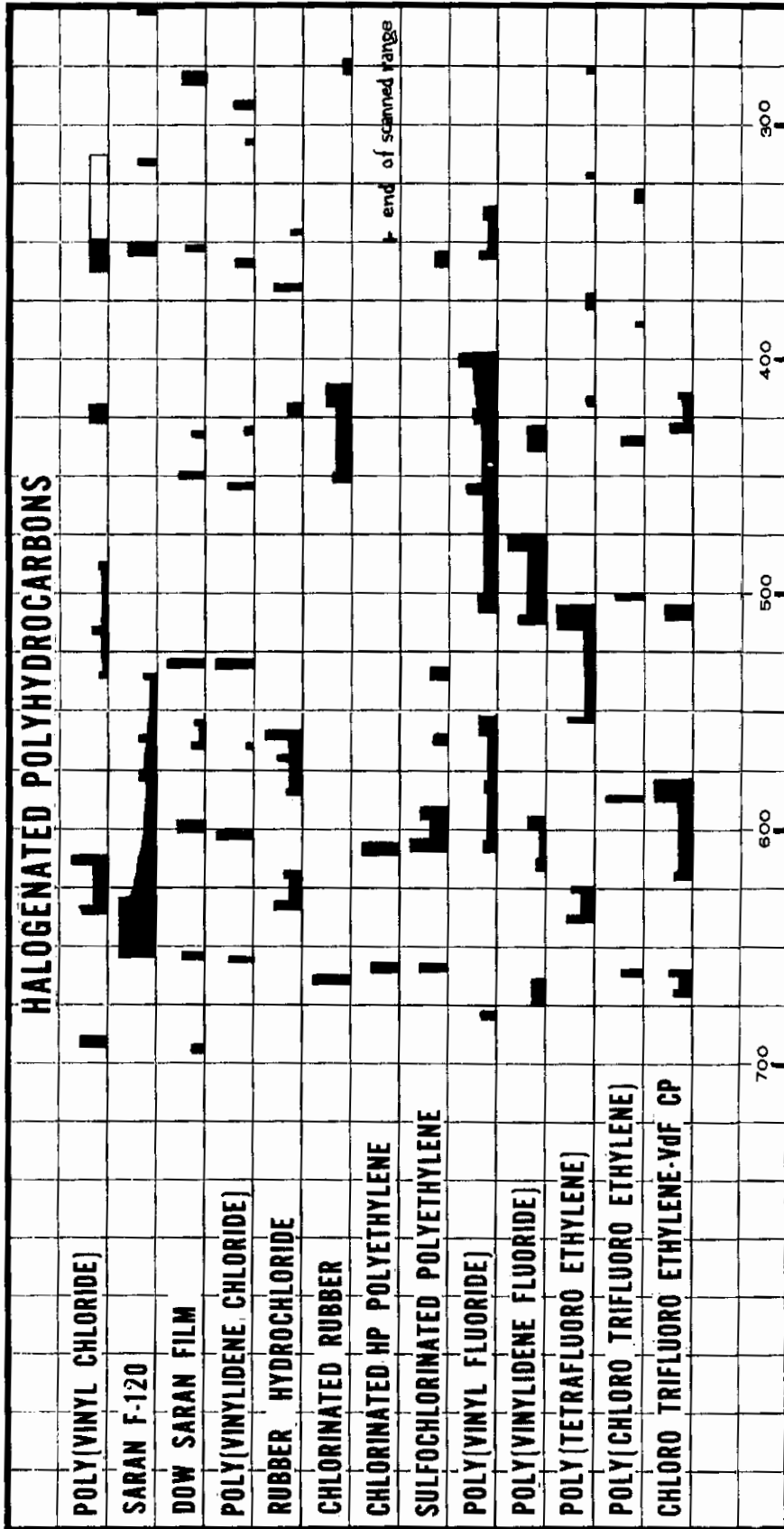


Chart III. - Absorption Frequencies of Halogenated Polyhydrocarbons

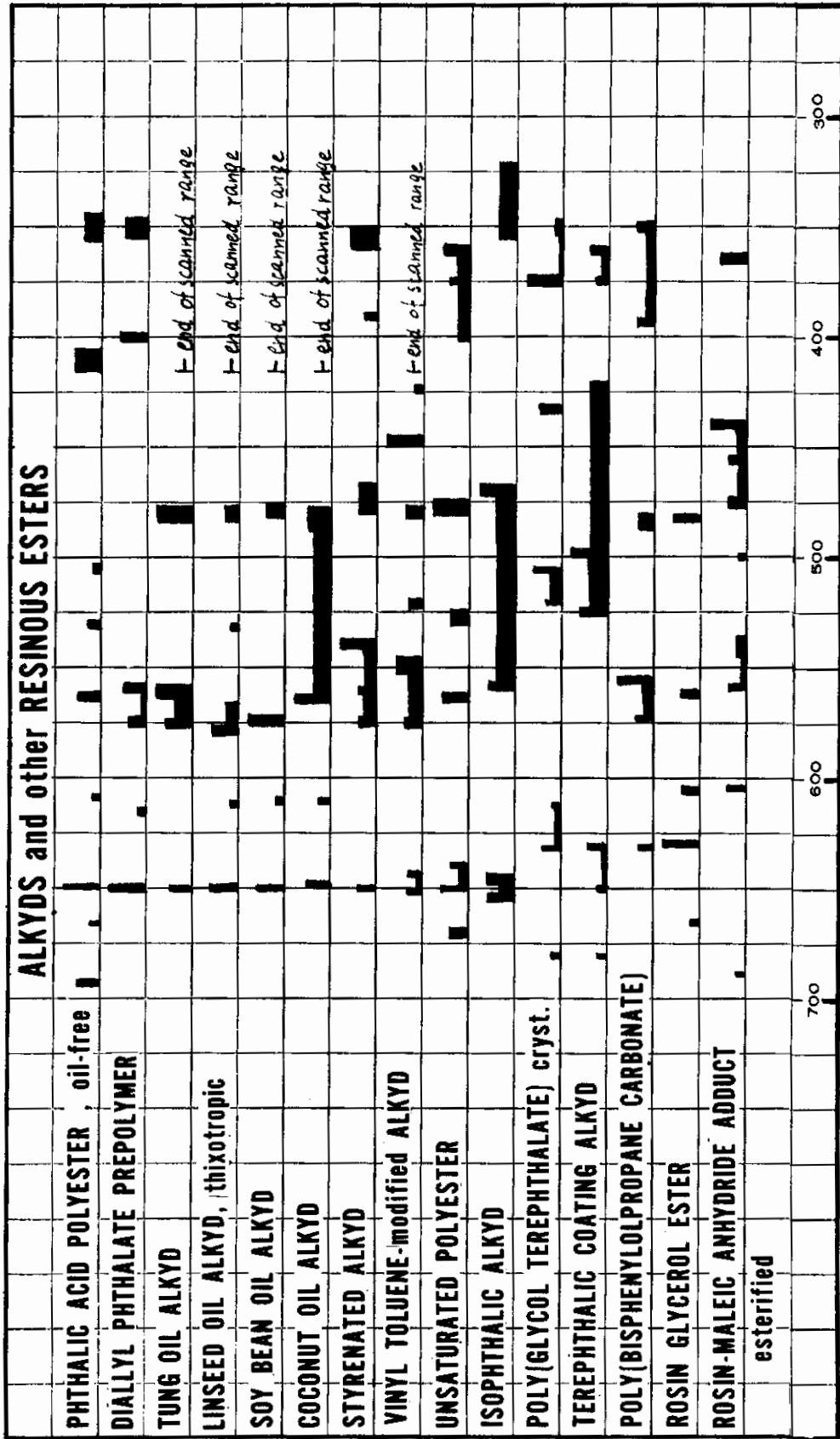


Chart IV. - Absorption Frequencies of Alkyds and Other Resinous Esters

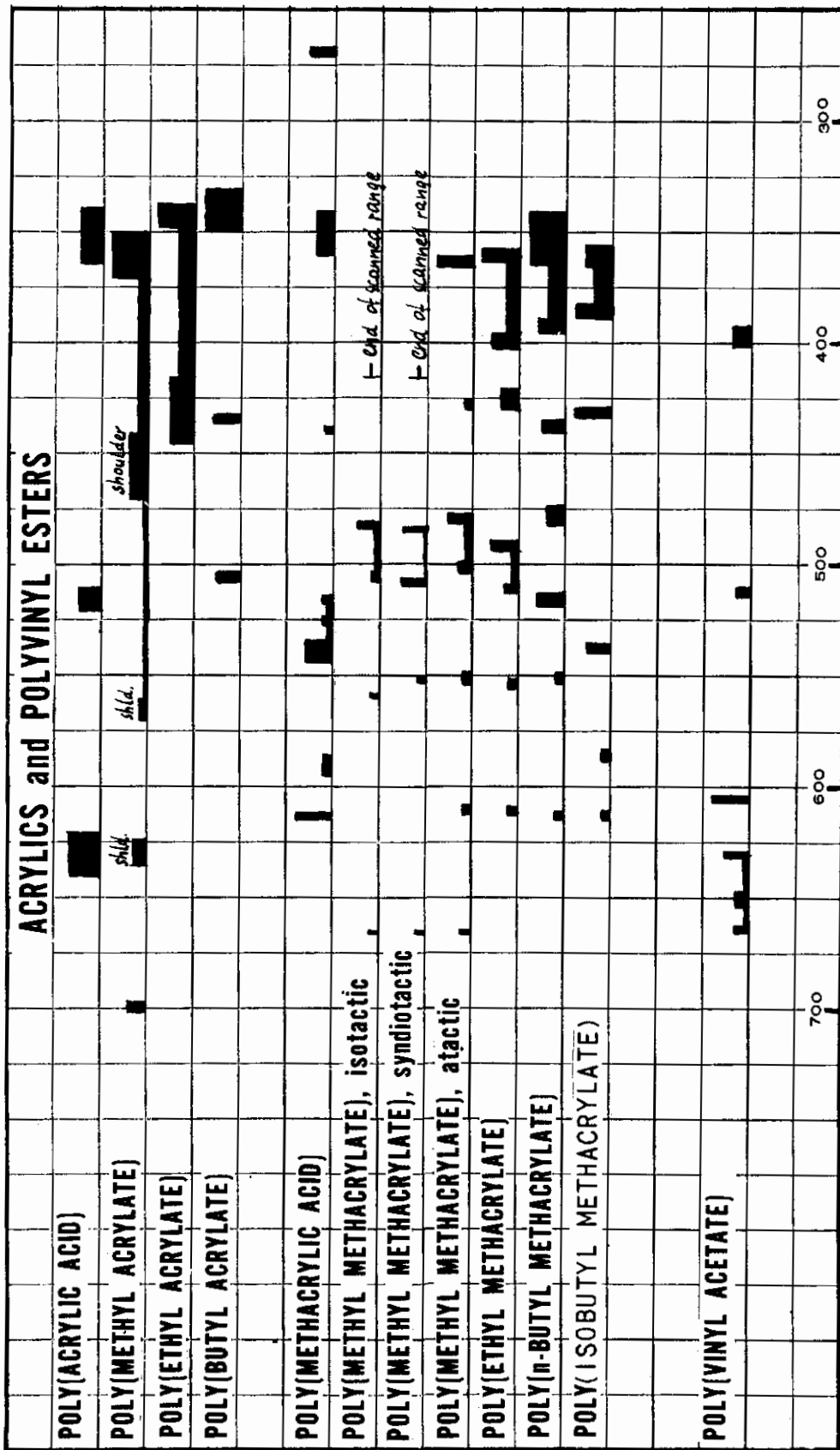


Chart V. - Absorption Frequencies of Acrylics and Polyvinyl Esters

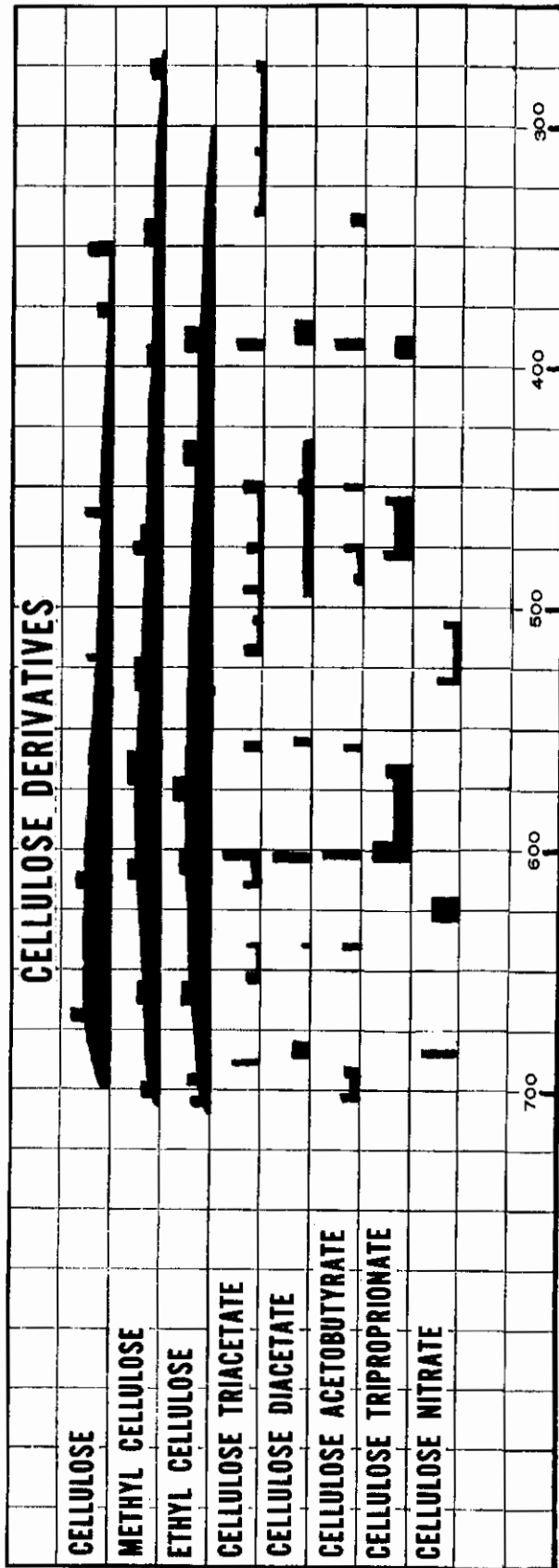


Chart VI. - Absorption Frequencies of Cellulose Derivatives

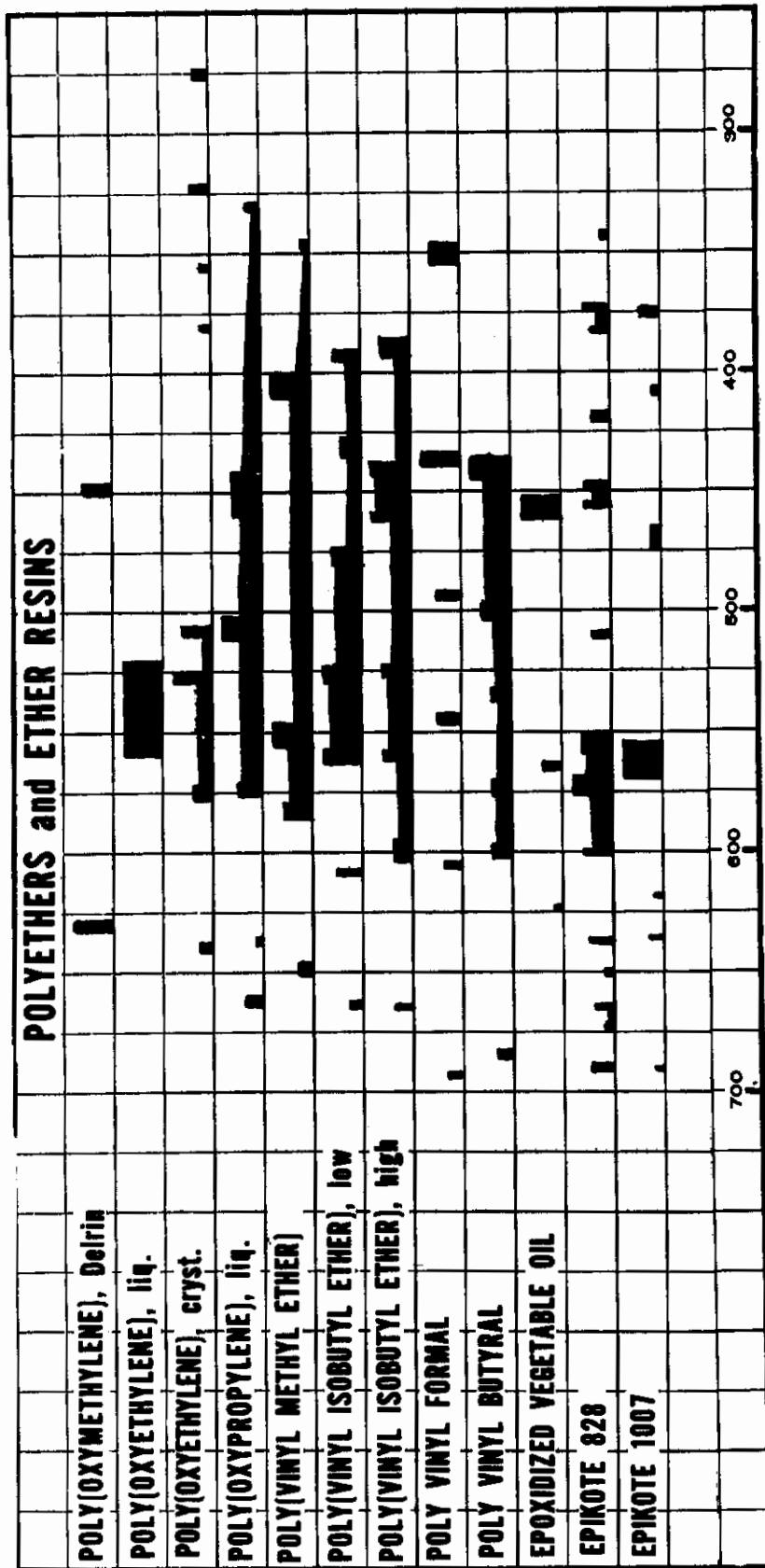


Chart VII. - Absorption Frequencies of Polyethers and Ether Resins



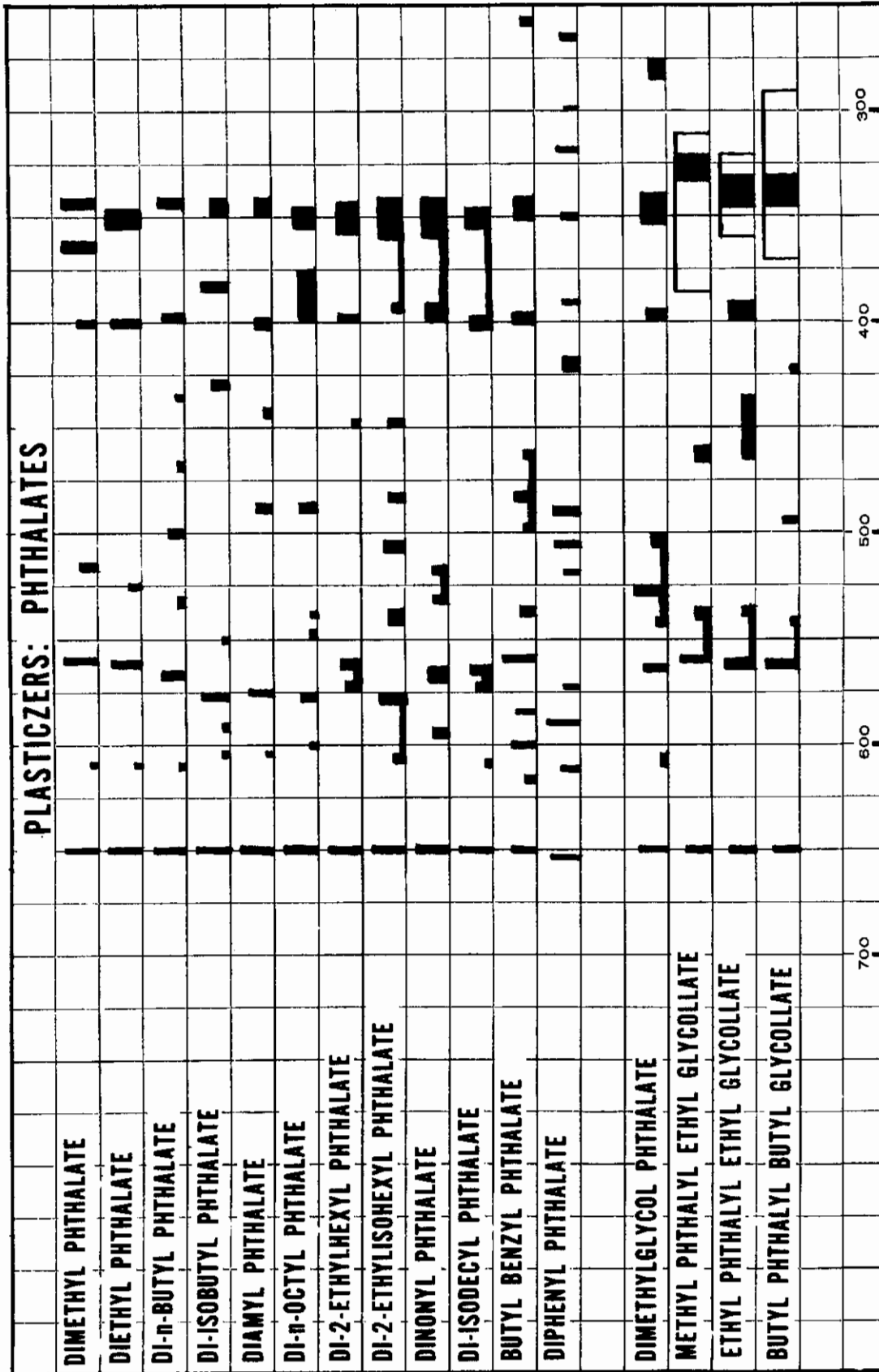


Chart IX. - Absorption Frequencies of Plasticizers: Phthalates



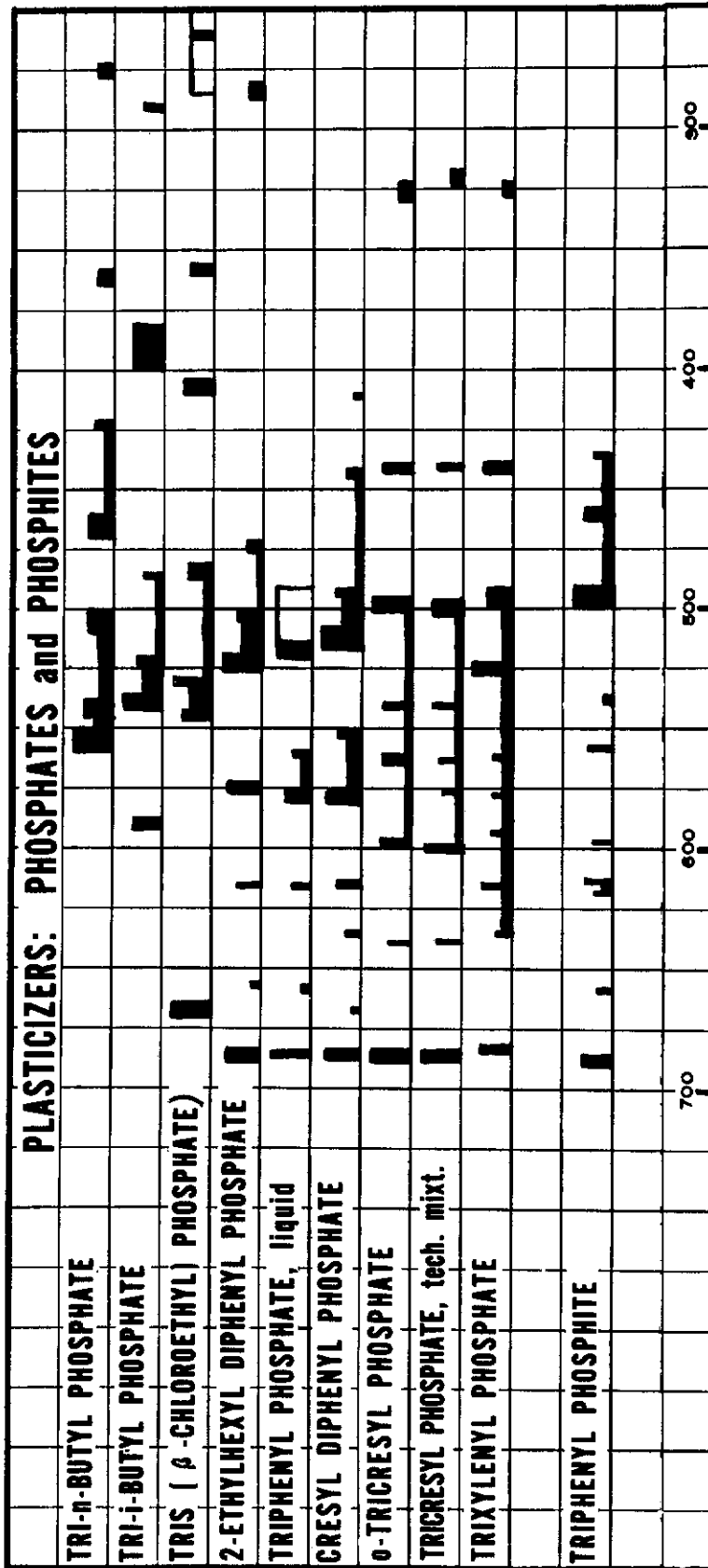


Chart X. - Absorption Frequencies of Plasticizers: Phosphates and Phosphites

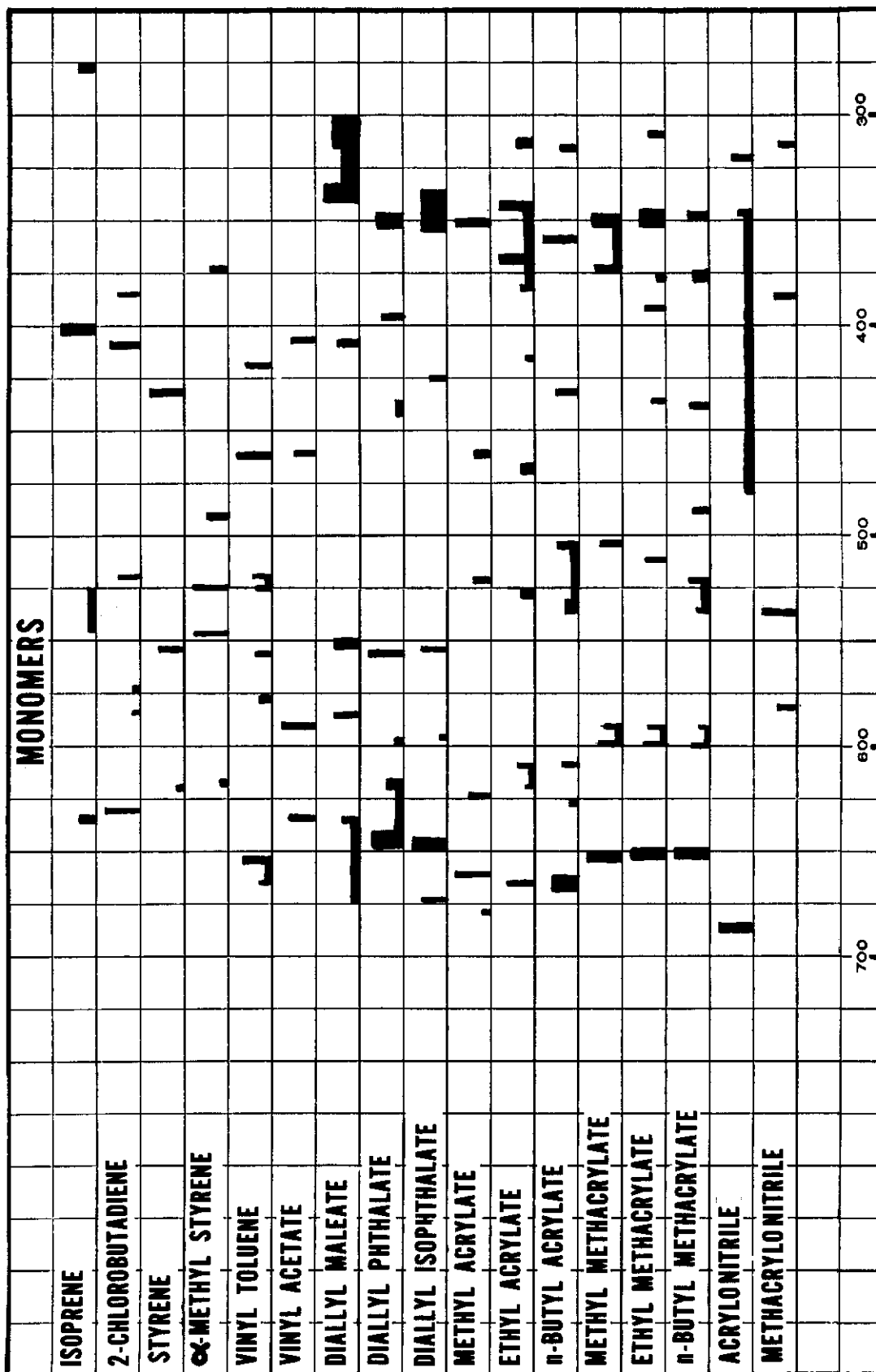


Chart XI. - Absorption Frequencies of Monomers